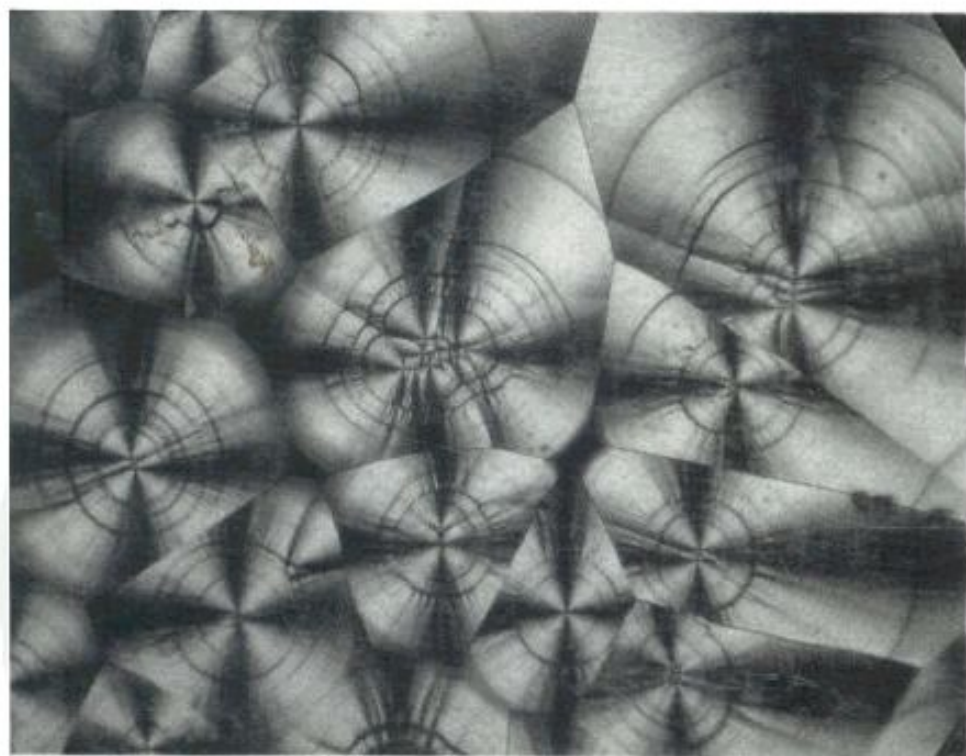


HANDBOOK OF CHEMICAL VAPOR DEPOSITION

Principles, Technology and Applications

SECOND EDITION



by
Hugh O. Pierson

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HANDBOOK OF CHEMICAL VAPOR DEPOSITION (CVD)

Principles, Technology, and Applications

Second Edition

by

Hugh O. Pierson

Consultant and Sandia National Laboratories (retired)
Albuquerque, New Mexico

**NOYES PUBLICATIONS
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Preface to the First Edition

Chemical vapor deposition (CVD) has grown very rapidly in the last twenty years and applications of this fabrication process are now key elements in many industrial products, such as semiconductors, optoelectronics, optics, cutting tools, refractory fibers, filters and many others. CVD is no longer a laboratory curiosity but a major technology on par with other major technological disciplines such as electrodeposition, powder metallurgy, or conventional ceramic processing.

The estimated market for CVD products is very large and predicted to reach almost three billion dollars in 1993, in the U.S. alone. The rapid development of the technology and the expansion of the market are expected to continue in the foreseeable future.

The reasons for the success of CVD are simple:

- CVD is a relatively uncomplicated and flexible technology which can accommodate many variations.
- With CVD, it is possible to coat almost any shape of almost any size.
- Unlike other thin film techniques such as sputtering CVD can also be used to produce fibers, monoliths, foams and powders.
- CVD is economically competitive.

Still the technology faces many challenges and a large research and development effort is under way in most major laboratories in the U.S., Japan and Europe, particularly in the semiconductor and tool industries. The general outlook is one of constant change as new designs, new products and new materials are continuously being introduced.

Generally CVD is a captive operation and an integral part of a fabrication process, particularly in microelectronics where most manufacturers have their own CVD facilities. It is also an international business, and, while the U.S. is still in the lead, a great deal of work is under way, mostly in Japan and Europe. A significant trend is the internationalization of the CVD industry, with many multi-national ventures.

Several books have recently been published on the subject of CVD, each dealing with a specific aspect of the technology, such as CVD for microelectronics or metallo-organic CVD. With many of his colleagues, the author has felt the need for a general, systematic, objective, and balanced review solely devoted to CVD, which would cover all its scientific, engineering, and applications aspects, coordinate the divergent trends found today in the CVD business, promote interaction and sharpen the focus of research and development.

To fill this need is the purpose of this book, which should be useful to students, scientists, and engineers, as well as production and marketing managers and suppliers of materials, equipment and services.

The author is fortunate to have the opportunity, as a consultant, to review and study CVD processes, equipment, materials and applications for a wide cross-section of the industry, in the fields of optics, optoelectronics, metallurgy and others. He is in a position to retain an overall viewpoint difficult to obtain otherwise.

The book is divided into three major parts. The first covers a theoretical examination of the CVD process, a description of the major chemical reactions and a review of the CVD systems and equipment used in research and production, including the advanced subprocesses such as plasma, laser, and photon CVD.

The second part is a review of the materials deposited by CVD, i.e., metals, non-metallic elements, ceramics and semiconductors, and the reactions used in their deposition.

The third part identifies and describes the present and potential applications of CVD in semiconductors and electronics, in optics and optoelectronics, in the coating of tools, bearings and other wear- and corrosion-resistant products, and in the automobile, aerospace, and other major industries.

The author is indebted to Dr. Jacob Stiglich and other members of the staff at Ultramet for their cooperation, and to an old friend, Dr. John M. Blocher Jr., for his many ideas, comments and thorough review of the manuscript. He is also grateful to George Narita, Executive Editor of Noyes Publications, for his help and patience in the preparation of this book.

February 1992
Albuquerque, New Mexico

Hugh Pierson

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Preface to the Second Edition

Since the publication of the first edition of the *Handbook of Chemical Vapor Deposition* in early 1992, the technology has developed at a rapid rate and the number and scope of its applications and their impact of the market have increased considerably. The size of the CVD market today (1998) is estimated to be at least double that of the market six years ago. These factors led to the need to revise and expand the first edition of the Handbook.

Two major contributors to this rapid growth are plasma CVD and metallo-organic CVD (MOCVD). Both are extensively reviewed in this new edition. Likewise, the growing importance of CVD in the production of semiconductor and related applications is emphasized with a systematic and detailed analysis of the role of CVD in this field.

Also noted is the rapid expansion of a number of materials produced by CVD, which include copper, tungsten, diamond, silicon carbide, silicon nitride, titanium nitride, and others. The coverage of the chemistry and deposition techniques of these materials has been greatly expanded.

December 1997
Sandia Park, New Mexico

Hugh Pierson

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Conversion Guide

Units in this book conform to the SI system (Système International d'Unités). They are listed in the following tables with the relevant conversion factors.

Table 1
Base and Derived SI Units

Physical Quantity	Name	Symbol
Base Units		
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric Current	ampere	A
Thermodynamic Temperature	kelvin	K
Amount of Substance	mole	mol
Derived Units		
Frequency	hertz	Hz
Energy	joule	J
Force	newton	N
Power	watt	W
Pressure	pascal	Pa
Electric Potential Difference	volt	V
Electric Resistance	ohm	Ω

Table 2
Decimal Multiples and Submultiples

Prefix	Symbol	Multiple
Giga	G	10^9
Mega	M	10^6
Kilo	k	10^3
Deci	d	10^{-1}
Centi	c	10^{-2}
Milli	m	10^{-3}
Micro	μ	10^{-6}
Nano	n	10^{-9}
Pico	p	10^{-12}

Table 3
Conversion of Units to SI- and Related-Units

From	To	Multiply by
Length		
in	m	2.54×10^{-2}
ft	m	0.3048
angstrom	m	10^{-8}
angstrom	nm	10^{-1}
Area		
sq in	m^2	6.4516×10^{-4}
sq in	cm^2	6.4516
sq ft	m^2	9.2903×10^{-2}

(Cont'd)

Table 3 (*cont'd*)

Volume		
cu in	m ³	1.63871 x 10 ⁻⁵
cu ft	m ³	2.83168 x 10 ⁻²
liter	m ³	10 ⁻³
gal (US)	m ³	3.785 x 10 ⁻³

Mass and Mass per Volume

lb	kg	0.453 592
g/cm ³	kg m ⁻³	10 ³
lb/ft ³	kg m ⁻³	1.601 x 10 ¹
lb/in ³	kg m ⁻³	2.767 99 x 10 ⁴
lb/in ³	g cm ⁻³	2.767 99 x 10 ¹

Energy

btu	J	1.054 35
cal	J	4.1868
eV	J	1.602 10 x 10 ⁻¹⁹
kW h	J	3.6 x 10 ⁶

Force

kgf	N	9.806 65
lbf	N	4.448 22

Power

hp	W	7.457 x 10 ²
btu/h	W	2.928 75 x 10 ⁻¹

Pressure

mm Hg	Pa	1.333 22 x 10 ²
atm	Pa	1.01325 x 10 ⁵
in Hg (32°F)	Pa	3.386 38 x 10 ³
N m ⁻²	Pa	1

(*cont'd*)

Table 3 (*cont'd*)

Stress (force per unit area)

kg/mm ²	MPa	9.806 65
lb/in ² (psi)	MPa	6.894 75 x 10 ⁻³

Temperature

°F	°C	5/9 (°F - 32)
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Thermal Conductivity

J m ⁻¹ s ⁻¹ °C	W m ⁻¹ K	1
cal/cm sec °C	W m ⁻¹ K	4.185 x 10 ²
Btu/ft h °F	W m ⁻¹ K	1.730 73
Btu in/s ft ² °F	W m ⁻¹ K	5.192 20 x 10 ²

Thermal Expansion

in/in °C	m m ⁻¹ K	1
in/in °F	m m ⁻¹ K	1.8

Specific Heat (heat capacity)

btu/lb °F	J kg ⁻¹ K	4.186 80 x 10 ³
cal/g °C	J kg ⁻¹ K	4.186 60 x 10 ³

Introduction and General Considerations

1.0 INTRODUCTION

Chemical vapor deposition (CVD) is a versatile process suitable for the manufacturing of coatings, powders, fibers, and monolithic components. With CVD, it is possible to produce most metals, many nonmetallic elements such as carbon and silicon as well as a large number of compounds including carbides, nitrides, oxides, intermetallics, and many others. This technology is now an essential factor in the manufacture of semiconductors and other electronic components, in the coating of tools, bearings, and other wear-resistant parts and in many optical, optoelectronic and corrosion applications. The market for CVD products in the U.S. and abroad is expected to reach several billions dollars by the end of the century.

The wide range of CVD products is illustrated by the following recent commercial products (1997):

- Diffusion barrier layers for advanced semiconductor integrated circuits of titanium nitride deposited by metallo-organic CVD (MOCVD)
- Diamond-like carbon (DLC) coatings produced by plasma-CVD for bushings and textile components with much improved wear resistance.

- Titanium carbide and titanium nitride coatings for carbide tools that greatly outperform uncoated tools and are taking an increasing share of the market.
- Iridium, deposited by MOCVD, which has shown remarkable resistance to corrosion in small rocket nozzles at temperatures up to 2000°C.
- Metallization of semiconductors with copper deposited by MOCVD, replacing aluminum, minimizing electromigration. CVD is now the major process in the production of advanced semiconductor components.
- Energy saving optical coatings for architectural glass by atmospheric-pressure CVD, produced in situ during the processing of float glass.
- Pyrolytic boron-nitride crucibles produced by CVD with outstanding chemical inertness, which are used extensively in the electronic industry.
- CVD boron fibers which are extremely stiff and strong and are used as reinforcement in structural components in aerospace designs.
- High thermal conductivity CVD-diamond films deposited on heat spreaders or heat slugs to dissipate the heat of high-density integrated circuits.

1.1 Definition of CVD

Chemical vapor deposition may be defined as the deposition of a solid on a heated surface from a chemical reaction in the vapor phase. It belongs to the class of vapor-transfer processes which is atomistic in nature, that is the deposition species are atoms or molecules or a combination of these. Beside CVD, they include various physical-vapor-deposition processes (PVD) such as evaporation, sputtering, molecular-beam epitaxy, and ion plating.

In many respects, CVD competes directly with the PVD processes, but it is also used in conjunction with them and many of the newer processes are actually combinations of the two systems such as plasma-enhanced CVD or activated sputtering. A general knowledge of the PVD processes is important for the full understanding and appreciation of CVD and a summary description is given in Appendix A.

1.2 Advantages and Limitations of CVD

CVD has several important advantages which make it the preferred process in many cases. These can be summarized as follows:

- It is not restricted to a line-of-sight deposition which is a general characteristic of sputtering, evaporation and other PVD processes. As such, CVD has high throwing power. Deep recesses, holes, and other difficult three-dimensional configurations can usually be coated with relative ease. For instance, integrated circuit via holes with an aspect ratio of 10:1 can be completely filled with CVD tungsten.
- The deposition rate is high and thick coatings can be readily obtained (in some cases centimeters thick) and the process is generally competitive and, in some cases, more economical than the PVD processes.
- CVD equipment does not normally require ultrahigh vacuum and generally can be adapted to many process variations. Its flexibility is such that it allows many changes in composition during deposition and the codeposition of elements or compounds is readily achieved.

CVD however is not the universal coating panacea. It has several disadvantages, a major one being that it is most versatile at temperatures of 600°C and above; many substrates are not thermally stable at these temperatures. However, the development of plasma-CVD and metallo-organic CVD partially offsets this problem. Another disadvantage is the requirement of having chemical precursors (the starter materials) with high

vapor pressure which are often hazardous and at times extremely toxic. The by-products of the CVD reactions are also toxic and corrosive and must be neutralized, which may be a costly operation.

2.0 HISTORICAL PERSPECTIVE

CVD is not a new process. As stated in the pioneer work of Powell, Oxley, and Blocher,^[1] its first practical use was developed in the 1880s in the production of incandescent lamps to improve the strength of filaments by coating them with carbon or metal. In the same decade, the carbonyl process was developed by Ludwig Mond and others for the production of pure nickel. A number of patents were issued during that period covering the basis of CVD.^[2]

CVD developed slowly in the next fifty years and was limited mostly to extraction and pyrometallurgy for the production of high-purity refractory metals such as tantalum, titanium, and zirconium. Several classical CVD reactions were developed at that time including the carbonyl cycle (the Mond process), the iodide decomposition (the de Boer-Van Arkel process) and the magnesium-reduction reaction (the Kroll process).

At the end of World War II, CVD expanded rapidly as researchers realized its advantages for the production of coatings and freestanding shapes. Its importance has been growing ever since. Other important dates in the development of CVD are the following:

- 1960: Introduction of the terms *CVD* and *PVD* to distinguish “chemical vapor deposition” from “physical vapor deposition.”^[1]
- 1960: Introduction of CVD in semiconductor fabrication.
- 1960: CVD TiC coating on cemented carbide tools introduced and development of CVD tungsten.
- 1963: Introduction of plasma CVD in electronics.^[3]
- 1968: Start of industrial use of CVD coated cemented carbides.^[3]

- 1980s: Introduction of CVD diamond coatings.
- 1990s: Rapid expansion of metallo-organic CVD (MOCVD) for ceramic and metal deposition.
- 1990s: Development of cluster tools combining CVD, PVD and other processing steps in a single tool for semiconductor fabrication. Major development of CVD in optics and optoelectronics.

Today, the technology is developing at an increasingly rapid rate. However, to retain the right perspective, it should be noted that it took over a century of steady and continuous scientific and engineering efforts to reach the present state of the art. Yet, in spite of this progress, many formidable challenges remain, such as the accurate prediction of a given CVD composition and its structure and properties. In fact, even though the understanding of the theory and mechanism of CVD has made great advances, the process is still often considered as much an art as a science and progress continues to rely for a large part on experimental developments.

3.0 THE APPLICATIONS OF CVD

CVD is a versatile and dynamic technology which is constantly expanding and improving as witnessed by the recent developments in metallo-organic CVD, plasma CVD, and many others. As the technology is expanding, so is the scope of its applications. This expansion is the direct result of a large research effort carried out by many workers in universities, government laboratories and industry (especially the semiconductor industry). The outlook is one of constant changes as new designs, new products and new materials are continuously being introduced.

Two major areas of application of CVD have rapidly developed in the last twenty years or so, namely in the semiconductor industry and in the so-called metallurgical-coating industry which includes cutting-tool fabrication. CVD technology is particularly important in the production of semiconductors and related electronic components. It is by far the most

important area of CVD and is estimated to comprise three-quarters of all CVD production.

In this book, the CVD applications are classified by product functions such as electrical, opto-electrical, optical, mechanical and chemical. This classification corresponds roughly to the various segments of industry such as the electronic industry, the optical industry, the tool industry, and the chemical industry. CVD applications are also classified by product forms such as coatings, powders, fibers, monoliths, and composites.

Inevitably, there is a certain degree of overlapping between these two general classifications. For instance, CVD optical applications are found as both coatings and fibers while fibers are used in optics as well as in structural and mechanical applications. These relationships will be reviewed in the several chapters on applications.

4.0 PROFILE OF THE CVD BUSINESS

The principal objective of this book is the study of the CVD technology. However, it is also important to consider this technology within the more general context of the CVD industry and a brief review of the industry is necessary in order to bring the technology into proper focus.

4.1 CVD Research

The amount of research and development in CVD is considerable in the U.S. and abroad, not only in industry but also in universities and in many of the major government laboratories. Government sponsorship in most countries remains an important factor either in terms of funding or as a research leader. Organizations such as the Department of Defense (DOD), the Department of Energy (DOE), and NASA in the U.S., MITI and NIRIM in Japan, CNRS in France, and others elsewhere, play leading roles in the development of CVD.

4.2 Internationalization of the CVD/PVD Business

CVD is now truly an international business and no longer a U.S. monopoly. The U.S. is still in the lead followed by Japan and Europe with Pacific-Rim countries coming up fast. The business is going through rapid changes as companies are sold, partnership created and dissolved, international joint ventures started, and new production facilities built all over the world.

4.3 Captive Production

CVD production, both in the U.S. and abroad, is essentially captive; that is, the CVD processing is an integral part of sequential operations. This is particularly true in the field of semiconductor and microelectronics where most manufacturers have their own CVD facilities which, more often than not, are incorporated within a production line. Likewise, the manufacturers of cutting tools, turbine blades, and other components that require hard coatings also have their own CVD facilities. There are few independent CVD producers as such and these usually specialize in specific applications or rely on their expertise for research and development of new processes and materials.

4.4 The Cost of CVD

An accurate cost or add-on value of a CVD operation is often difficult to isolate from the overall production cost. For instance, the fabrication of semiconductor chips is a complicated and lengthy procedure which involves many steps, including lithography, cleaning, etching, and oxidation not to mention single-crystal silicon growth and preparation. CVD is an integral part of this fabrication sequence and is used extensively (and in some cases exclusively) in the production of insulating, conductive and semiconductor coatings. To compute its exact cost is complex. In addition, this cost may vary considerably from one application to another and from one manufacturer to another.

4.5 CVD Equipment

Until about 1980, CVD equipment was designed and built in-house and a CVD equipment industry essentially did not exist as such. Since then, there has been a considerable shift to standardized production equipment built by specialized equipment manufacturers. This is the result of the increasing sophistication and cost of the technology, particularly in semiconductor and microelectronic fabrication. The CVD equipment market is now of considerable size and is attracting a large number of companies. It is estimated to reach two billion dollars worldwide in 1997. The business is still led by the U.S. with an estimated share of slightly less than 50% in 1996. These figures actually become less relevant with the rapid internationalization of the industry. Large foreign companies now have branches and plants in the U.S. and many major U.S. producers maintain operations abroad. This appears to be the shape of the future.

4.6 CVD/PVD Integration

An important recent trend is the tendency for the two processes, CVD and PVD, to merge. For instance, CVD now makes extensive use of plasma (a physical phenomenon) and reactive PVD (evaporation or sputtering) occurs in a chemical environment. Much of the new equipment reflects this process integration in the concept of cluster tools which may incorporate CVD, etching, sputtering, and ion implantation in one piece of equipment.

4.7 Metallo-organic CVD and Plasma CVD

Metallo-organic CVD (MOCVD) and plasma CVD are developing rapidly, not only in the semiconductor-microelectronic area but also in hard coatings for erosion and wear applications since the lower deposition temperature now permits the use of a broader spectrum of substrates. Special emphasis has been given to these two areas in this second edition of the *CVD Handbook* (see Ch. 4 and 5).

5.0 BOOK OBJECTIVES

The objectives of this book are to:

- Review the theoretical aspects of CVD, i.e., chemical thermodynamics, kinetics, and gas dynamics.
- Provide a detailed assessment of the technology of CVD and its relation to the production of coatings, fibers, powders, and monolithic shapes.
- Describe the various processes and equipment used in R&D and production such as thermal CVD, plasma CVD, photo CVD, MOCVD, and others.
- Review the materials that can be produced by CVD.
- Identify and describe present and potential CVD applications.

The book is divided into three major sections. The first deals with theory and processes (Ch. 2–5), the second with the materials that can be produced by CVD (Ch. 6–12), and the third with the present and potential CVD applications (Ch. 13–19). These sections are cross-referenced to facilitate review and reduce duplication.

All units in this book are metric, specifically the International System of Units (SI) and a metric conversion guide is included at the end of the book.

6.0 BACKGROUND REFERENCES

The following is a partial lists of relevant periodicals and technical conferences related to CVD.

6.1 Periodicals

Acta Crystallographica

Applied Physics Letters

Carbon

Ceramic Bulletin

Ceramic Engineering and Science Proceedings

Japanese Journal of Applied Physics

Journal of the American Ceramic Society

Journal of the American Chemical Society

Journal of Applied Physics

Journal of CVD

Journal of the Ceramic Society of Japan

Journal of Crystal Growth

Journal of the Electro-Chemical Society

Journal of the Less-Common Metals

Journal of Materials Research

Journal of Thin Films

Journal of Vacuum Science and Technology

Materials and Manufacturing Processes

Materials Engineering

Materials Research Society Bulletin

Nature

SAMPE Journal

SAMPE Quarterly

SPIE Publications

Science

6.2 Conferences

- International Conferences on Chemical Vapor Deposition (CVD) of the Electrochemical Society (biennial).
- Composites and Advanced Ceramics Conferences of the American Ceramic Society (annual).
- Materials Research Society Conferences (annual).
- International Conference on Surface Modification Technologies (annual).

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1. Powell, C. F., "Chemical Vapor Deposition," in *Vapor Deposition* (C. F. Powell, J. H. Oxley and J. M. Blocher, Jr., eds.), pp. 249–276, John Wiley & Sons, New York (1966)
2. Sawyer, W. E., and Man, A., U.S. Pat. 229335 (June 29, 1880) on pyrolytic carbon; Aylsworth, J. W., U.S. Pat. 553296 (Jan. 21, 1896) on metal deposition; deLodyguine, A., U.S. Pat. 575002 (Jan. 12, 1897) and 575668 (Jan. 19, 1897) on metal deposition; Mond, L., U.S. Pat. 455230 (June 30, 1891) on nickel deposition
3. Ruppert, W., U.S. Patent 2962388
4. Atl, L. L., et al., *J. Electrochemical Soc.*, 110:456 (1963) and 111:120 (1964)

Fundamentals of Chemical Vapor Deposition

1.0 INTRODUCTION

Chemical vapor deposition is a synthesis process in which the chemical constituents react in the vapor phase near or on a heated substrate to form a solid deposit. The CVD technology combines several scientific and engineering disciplines including thermodynamics, plasma physics, kinetics, fluid dynamics, and of course chemistry. In this chapter, the fundamental aspects of these disciplines and their relationship will be examined as they relate to CVD.

The number of chemical reactions used in CVD is considerable and include thermal decomposition (pyrolysis), reduction, hydrolysis, disproportionation, oxidation, carburization, and nitridation. They can be used either singly or in combination (see Ch. 3 and 4). These reactions can be activated by several methods which are reviewed in Ch. 5. The most important are as follows:

- Thermal activation which typically takes place at high temperatures, i.e., $>900^{\circ}\text{C}$, although the temperature can also be lowered considerably if metallo-organic precursors are used (MOCVD).

- Plasma activation which typically takes place at much lower temperatures, i.e., 300–500°C.
- Photon activation, usually with shortwave ultraviolet radiation, which can occur by the direct activation of a reactant or by the activation of an intermediate .

Until recently, most CVD operations were relatively simple and could be readily optimized experimentally by changing the reaction chemistry, the activation method, or the deposition variables until a satisfactory deposit was achieved. It is still possible to do just that and in some cases it is the most efficient way to proceed. However, many of the CVD processes are becoming increasingly complicated with much more exacting requirements, which would make the empirical approach too cumbersome.

1.1 Theoretical Analysis

A theoretical analysis is, in most cases, an essential step which, if properly carried out, should predict any of the following:

- Chemistry of the reaction (intermediate steps, by-products).
- Reaction mechanism.
- Composition of the deposit (i.e., stoichiometry).
- Structure of the deposit (i.e., the geometric arrangement of its atoms).

This analysis may then provide a guideline for an experimental program and considerably reduce its scope and save a great deal of time and effort.

Such an analysis requires a clear understanding of the CVD process and a review of several fundamental considerations in the disciplines of thermodynamics, kinetics, and chemistry is in order. It is not the intent here to dwell in detail on these considerations but rather provide an overview which should be generally adequate. More detailed investigations of the theoretical aspects of CVD are given in Refs. 1–3.

2.0 THERMODYNAMICS OF CVD

A CVD reaction is governed by *thermodynamics*, that is the driving force which indicates the direction the reaction is going to proceed (if at all), and by *kinetics*, which defines the transport process and determines the rate-control mechanism, in other words, how fast it is going.

Chemical thermodynamics is concerned with the interrelation of various forms of energy and the transfer of energy from one chemical system to another in accordance with the first and second laws of thermodynamics. In the case of CVD, this transfer occurs when the gaseous compounds, introduced in the deposition chamber, react to form the solid deposit and by-products gases.

2.1 ΔG Calculations and Reaction Feasibility

The first step of a theoretical analysis is to ensure that the desired CVD reaction will take place. This will happen if the thermodynamics is favorable, that is if the transfer of energy—the free-energy change of the reaction known as ΔG_r —is negative. To calculate ΔG_r , it is necessary to know the thermodynamic properties of each component, specifically their free energies of formation (also known as Gibbs free energy), ΔG_f . The relationship is expressed by the following equation:

$$\text{Eq. (1)} \quad \Delta G_r^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

The free energy of formation is not a fixed value but varies as a function of several parameters which include the type of reactants, the molar ratio of these reactants, the process temperature, and the process pressure. This relationship is represented by the following equation:

$$\text{Eq. (2)} \quad \Delta G_r = \Delta G_f^o + RT \ln Q$$

where: $\Delta G_r^o = \sum z_i^i \Delta G_{f,i}^o$
 z_i = stoichiometric coefficient of species “i” in the CVD reaction (negative for reactants, positive for products)

$\Delta G_{f,i}^o$ = standard free energy of formation of species “i” at temperature T and 1 atm.

R = gas constant

T = absolute temperature

$$Q = \prod_i a_i^{z_i}$$

a_i = activity of species “i” which is = 1 for pure solids and = $p_i = x_i P_T$ for gases

p_i = partial pressure of species “i”

x_i = mole fraction of species “i”

P_T = total pressure

By definition, the free energy change for a reaction at equilibrium is zero, hence:

$$\text{Eq. (3)} \quad \Delta G = - RT \ln K$$

(K is the equilibrium constant)

It is the equilibrium conditions of composition and activities (partial pressure for gases) that are calculated to assess the yield of a desired reaction.

A demonstration of the feasibility of a reaction is illustrated in the following example regarding the formation of titanium diboride using either diborane or boron trichloride as a boron source, as shown in the following reactions:



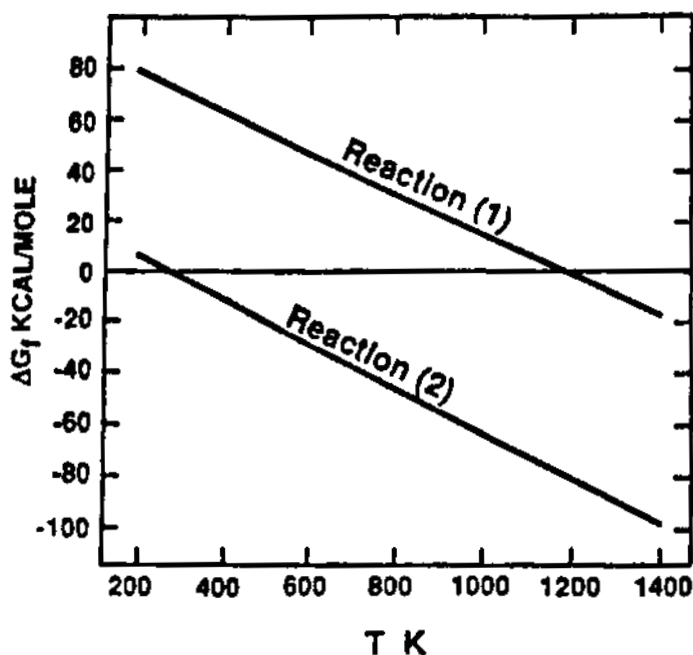


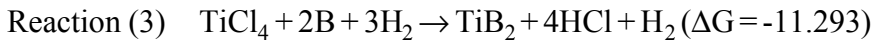
Figure 2.1. Changes in free energy of formation for TiB_2 deposition in the following reactions: (1) $\text{TiCl}_4 + 2\text{BCl}_3 \rightarrow \text{TiB}_2 + 10\text{HCl}$; (2) $\text{TiCl}_4 + \text{B}_2\text{H}_6 \rightarrow \text{TiB}_2 + \text{H}_2$.

The changes in free energy of formation of Reaction (1) are shown in Fig. 2.1 as a function of temperature.^[4] The values of ΔG_r were calculated using Eq. (1) above for each temperature. The Gibbs free-energy values of the reactants and products were obtained from the JANAF Tables.^[5] Other sources of thermodynamic data are listed in Ref. 6. These sources are generally accurate and satisfactory for the thermodynamic calculations of most CVD reactions; they are often revised and expanded.

TiB_2 can also be obtained using diborane as a boron source as follows:



The changes in the free energy of formation on this reaction are shown in Fig. 2.1. It should be noted that the negative free energy change is a valid criterion for the feasibility of a reaction only if the reaction, as written, contains the major species that exist at equilibrium. In the case of Reaction (2), it is possible that B_2H_6 has already decomposed to boron and hydrogen and the equilibrium of the reaction might be closer to:



As can be seen in Fig. 2.1, if the temperature is raised sufficiently, ΔG_r becomes negative and the diborane reaction proceeds at a much lower temperature than the boron trichloride reaction.

2.2 Thermodynamic Equilibrium and Computer Programs

Reactions (1) and (2) above are actually greatly simplified. In reality, it is likely that subchlorides such as $TiCl_3$ and $TiCl_2$ will be formed in Reaction (1) and higher boranes in Reaction (2). Such factors are not revealed by the simple free-energy change calculations.

In many cases, a more complete understanding of CVD reactions and a better prediction of the results are needed and a more thorough thermodynamic and kinetic investigation is necessary. This is accomplished by the calculation of the thermodynamic equilibrium of a CVD system, which will provide useful information on the characteristics and behavior of the reaction, including the optimum range of deposition conditions.

The calculation is based on the rule of thermodynamics, which states that a system will be in equilibrium when the Gibbs free energy is at a minimum.^[7] The objective then is the minimization of the total free energy of the system and the calculation of equilibria at constant temperature and volume or at constant pressure.^[8] It is a complicated and lengthy calculation but, fortunately, several computer programs are now available that considerably simplify the task.^[9]

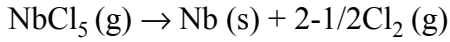
Such programs include SOLGASMIX, which was developed by Erikson and Besmann^{[10][11]} and EKVICALC and EKVIBASE, developed by Nolang.^[12] These programs are now used widely in equilibrium calculations in CVD systems. To operate them, it is first necessary to identify all the possible chemical species, whether gaseous or condensed phases, that might be found in a given reaction. The relevant thermodynamic properties of these phases are then entered in the program as input data. If properly performed, these calculations will provide the following information:

- The composition and amount of deposited material that is theoretically possible under any given set of deposition conditions, that is at a given temperature, a given pressure and given input concentration of reactants.
- The existence of gaseous species and their equilibrium partial pressures.
- The possibility of multiple reactions and the number and composition of possible solid phases, with the inclusion of the substrate as a possible reactant.
- The likelihood of a reaction between the substrate and the gaseous or solid species.

All of this is valuable information, which can be of great help. Yet, it must be treated with caution since, in spite of all the progress in thermodynamic analysis, the complexity of many CVD reactions, is such that predictions based on thermodynamic calculations, are still subject to uncertainty. As stated above, these calculations are based on chemical equilibrium which is rarely attained in CVD reactions.

It follows that, in order to provide a reliable and balanced investigation, it is preferable to combine the theoretical calculations with an experimental program and, hopefully, they will correlate. Fortunately, laboratory CVD experiments are relatively easy to design and carry out; they do not require expensive equipment and results can usually be obtained quickly and reliably.

A classic example, combining theoretical study and laboratory experiments, is the deposition of niobium, originally described by Blocher.^[13] The following reaction was used:



In Fig. 2.2, the critical deposition temperature of NbCl_5 , as a function of its initial pressure, is shown from experimental data from Blocher and the author. There are two temperature-pressure regions, which are separated by a straight line. The metal is deposited only in the region below the line. Above, there is no deposition. The line is a least-square fit of the data. Its position was confirmed using the SOLGASMIX computer program.

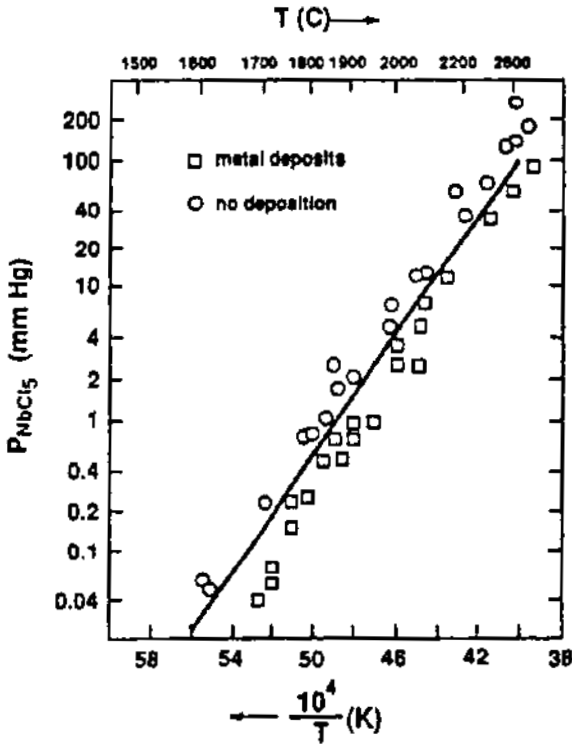


Figure 2.2. Critical deposition temperature of niobium as a function of NbCl_5 initial pressure.

This example shows the great degree of flexibility that can be obtained in CVD if a proper understanding of the thermodynamics and kinetics is gained. In this particular case, it was possible to deposit a uniform layer of NbC on a graphite rod simply by limiting the reaction to the deposition of the metal. Since the carbide could only be formed using the substrate as a carbon source, the rate was controlled by the diffusion rate of the carbon through the coating and deposition uniformity was achieved over the length of the graphite rod.

3.0 KINETICS AND MASS-TRANSPORT MECHANISMS

3.1 Deposition Sequence

As shown above, a thermodynamic analysis indicates what to expect from the reactants as they reach the deposition surface at a given temperature. The question now is, how do these reactants reach that deposition surface? In other words, what is the mass-transport mechanism? The answer to this question is important since the phenomena involved determines the reaction rate and the design and optimization of the CVD reactor.

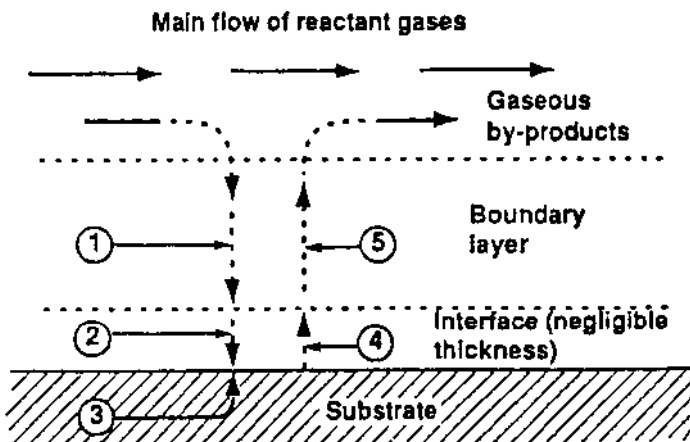
It should be first realized that any CVD process is subject to complicated fluid dynamics. The fluid, in this case a combination of gases, is forced through pipes, valves, and various chambers and, at the same time, is the object of large variations in temperature and to a lesser degree of pressure before it comes in contact with the substrate where the deposition reaction takes place. The reaction is heterogeneous which means that it involves a change of state, in this case from gaseous to solid.

In some cases, the reaction may take place before the substrate is reached while still in the gas phase (gas-phase precipitation) as will be reviewed later. As can be expected, the mathematical modeling of these phenomena can be complicated.

The sequence of events taking place during a CVD reaction is shown graphically in Fig. 2.3 and can be summarized as follows:^[1]

- Reactant gases enter the reactor by forced flow.
- Gases diffuse through the boundary layer.
- Gases come in contact with surface of substrate.
- Deposition reaction takes place on surface of substrate.
- Gaseous by-products of the reaction are diffused away from the surface, through the boundary layer.

These steps occur in the sequence shown and the slowest step determines the deposition rate. The rules of the boundary layer apply in most CVD depositions in the viscous flow range where pressure is relatively high. In cases where very low pressure is used (i.e., in the mTorr range), the rules are no longer applicable.

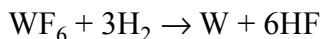


1. Diffusion in of reactants through boundary layer
2. Adsorption of reactants on substrate
3. Chemical reaction takes place
4. Desorption of adsorbed species
5. Diffusion out of by-products

Figure 2.3. Sequence of events during deposition.

3.2 Deposition in a CVD Flow Reactor

The sequence of events described above occurs at any given spot in a CVD flow reactor. As an example, one can consider the deposition of tungsten on the interior wall of a graphite tube by the hydrogen reduction of the fluoride as follows:



As shown schematically in Fig. 2.4a, the reactant gases are introduced in the upstream side, then flow down the reactor tube, and exhaust downstream through the vacuum pump.

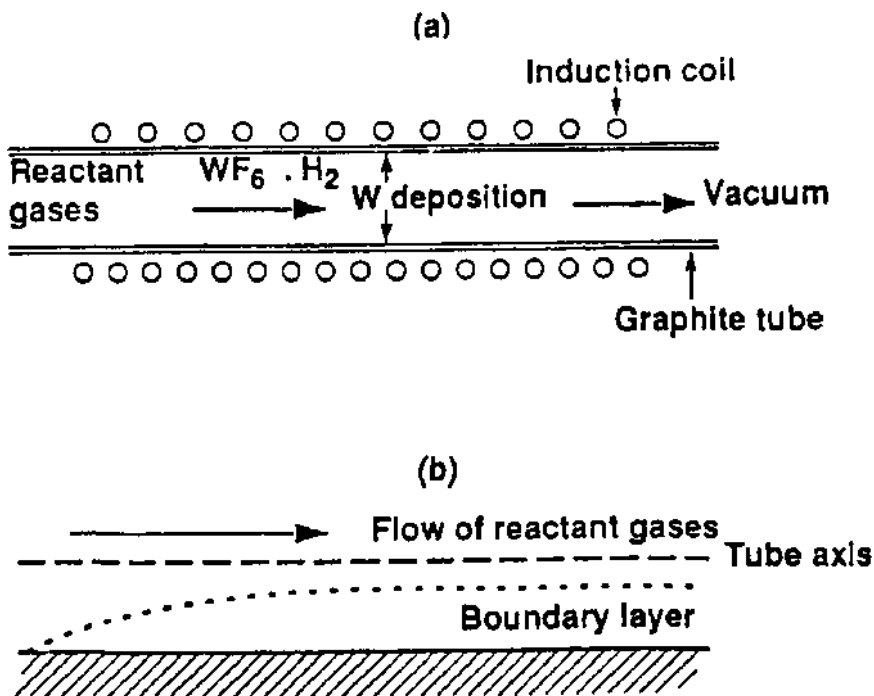


Figure 2.4. (a) Tungsten deposition in a tubular reactor, (b) boundary layer conditions.

3.3 Boundary Layer

The behavior of the gas as it flows down the tube is controlled by fluid mechanics and a complete investigation would be lengthy and outside the scope of this book. It is enough to say that the Reynolds number, R_e , which is a dimensionless parameter that characterizes the flow of a fluid, is such that the gas flow is generally laminar, although in some instances the laminar flow may be disturbed by convective-gas motion and may become turbulent.

In the case of laminar flow, the velocity of the gas at the deposition surface (the inner wall of the tube) is zero. The boundary is that region in which the flow velocity changes from zero at the wall to essentially that of the bulk gas away from the wall. This boundary layer starts at the inlet of the tube and increases in thickness until the flow becomes stabilized as shown in Fig. 2.4b. The reactant gases flowing above the boundary layer have to diffuse through this layer to reach the deposition surface as is shown in Fig. 2.3.

The thickness of the boundary layer, Δ , is inversely proportional to the square root of the Reynolds number as follows:

$$\text{Eq. (4)} \quad \Delta = \sqrt{\frac{x}{R_e}}$$

$$\text{where: } R_e = \frac{\rho u_x}{\mu}$$

ρ = mass density

u = flow density

x = distance from inlet in flow direction

μ = viscosity

This means that the thickness of the boundary layer increases with lower gas-flow velocity and with increased distance from the tube inlet.^[14]

3.4 Gas Velocity

Under such conditions, it is possible to obtain an approximate visualization of the gas-flow pattern by using TiO_2 smoke (generated when titanium chloride comes in contact with moist air), although thermal diffusion may keep the smoke particles away from the hot surface where a steep temperature gradient exists. Figure 2.5 shows a typical velocity pattern in a horizontal tube. As mentioned above, a steep velocity gradient is noticeable going from maximum velocity at the center of the tube to zero velocity at the surface of the wall. The gradient is also shallow at the entrance of the tube and increases gradually toward downstream.

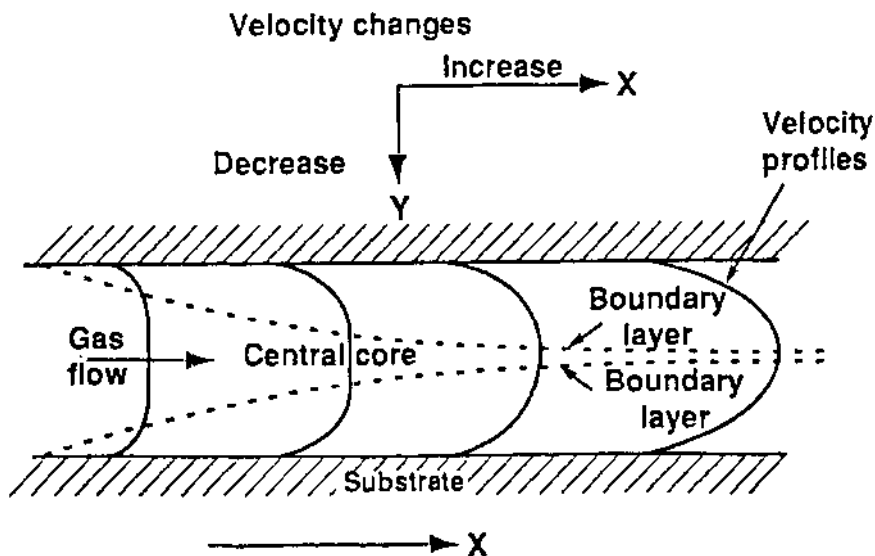


Figure 2.5. Boundary layer and velocity changes in a tube reactor, showing the graphs of velocity recorded at different positions on the tube.

3.5 Temperature

Figure 2.6 shows a typical temperature profile.^[2] The temperature boundary layer is similar to the velocity layer. The flowing gases heat rapidly as they come in contact with the hot surface of the tube, resulting in a steep temperature gradient. The average temperature increases toward downstream.

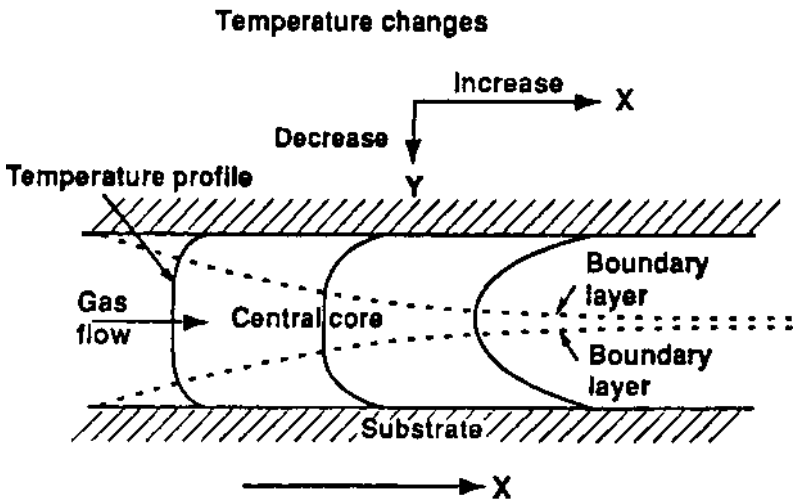


Figure 2.6. Temperature boundary layer and temperature changes in a tubular reactor, showing the graphs of temperature recorded at different positions on the tube.

3.6 Reactant-Gas Concentration

As the gases flow down the tube, they become gradually depleted as tungsten is deposited and the amount of the by-product gas, HF, increases in the boundary layer. This means that, at some point downstream, deposition will cease altogether when WF_6 is no longer present. The reactant concentration is illustrated in Fig. 2.7.

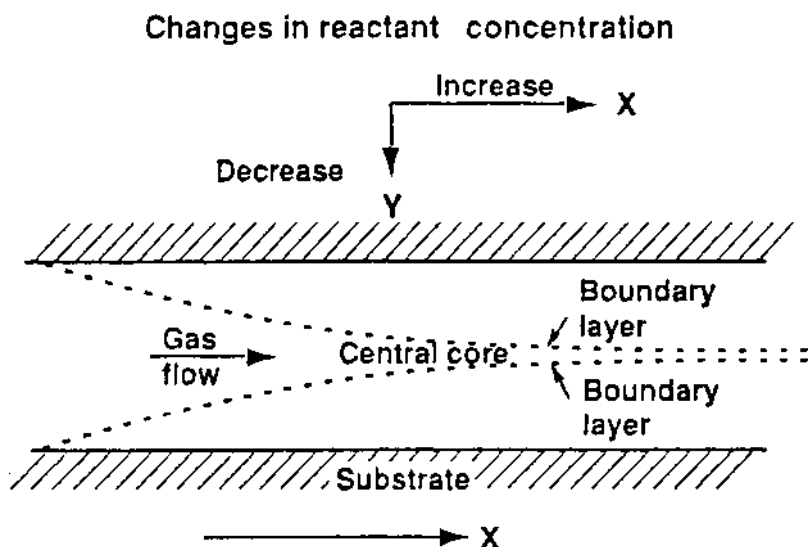


Figure 2.7. Changes in reactant concentration in a tubular reactor.

The boundary layers for these three variables (gas velocity, temperature, and concentration) may sometimes coincide, although in slow reactions, the profiles of velocity and temperature may be fully developed at an early stage while the deposition reaction is spread far downstream the tube.

As can be seen, conditions in a flowing reactor, even the simplest such as a tube, may be far from the thermodynamic equilibrium conditions predicted by the equilibrium computer programs. However, in the diffusion controlled range, it is possible to use as the driving force for diffusion, the difference between an assumed equi-

librium composition at the wall and the bulk-gas composition in the feed (adjusted for downstream depletion), to model some systems to a first approximation.

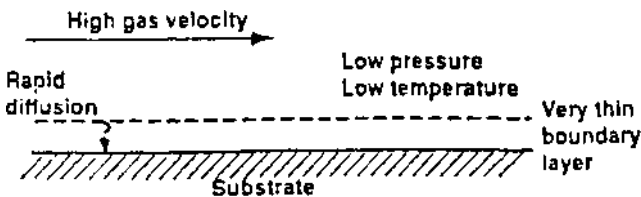
3.7 Rate-Limiting Steps

What is the rate limiting step of a CVD reaction? In other words, what factor controls the growth rate of the deposit? The answer to this question is critical since it will help to optimize the deposition reaction, obtain the fastest growth rate and, to some degree, control the nature of the deposit.

The rate-limiting step is generally determined by either the surface reaction kinetics or by mass transport.

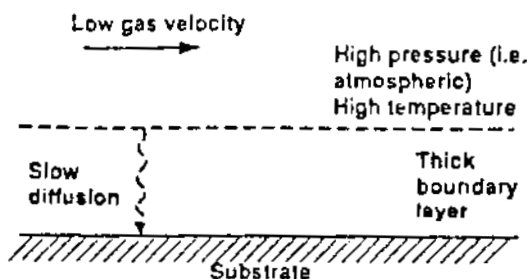
3.8 Surface-Reaction Kinetics

In the case of control by surface reaction kinetics, the rate is dependent on the amount of reactant gases available. As an example, one can visualize a CVD system where the temperature and the pressure are low. This means that the reaction occurs slowly because of the low temperature and there is a surplus of reactants at the surface since, because of the low pressure, the boundary layer is thin, the diffusion coefficients are large, and the reactants reach the deposition surface with ease as shown in Fig. 2.8a.



(a)

Figure 2.8. Rate-limiting steps in a CVD reaction (a) surface reaction kinetics control, (b) diffusion control.



(b)

Figure 2.8. (*Cont'd.*)

3.9 Mass Transport

When the process is limited by mass-transport phenomena, the controlling factors are the diffusion rate of the reactant through the boundary layer and the diffusion out through this layer of the gaseous by-products. This usually happens when pressure and temperature are high. As a result, the gas velocity is low as was shown above, and the boundary layer is thicker making it more difficult for the reactants to reach the deposition surface. Furthermore, the decomposition reaction occurs more rapidly since the temperature is higher and any molecule that reaches the surface reacts instantly. The diffusion rate through the boundary layer then becomes the rate limiting step as shown in Fig. 2.8b.

3.10 Control of Limiting Step

To summarize, the surface kinetics (or near surface kinetics) is the limiting step at lower temperature and diffusion is the rate limiting step at higher temperature. It is possible to switch from one rate-limiting step to the other by changing the temperature. This is illustrated in Fig. 2.9, where the Arrhenius plot (logarithm of the deposition rate vs. the reciprocal temperature) is shown for several reactions leading to the deposition of silicon,

using either SiH_4 , SiH_2Cl_2 , SiHCl_3 , or SiCl_4 as silicon sources in a hydrogen atmosphere.^[15]

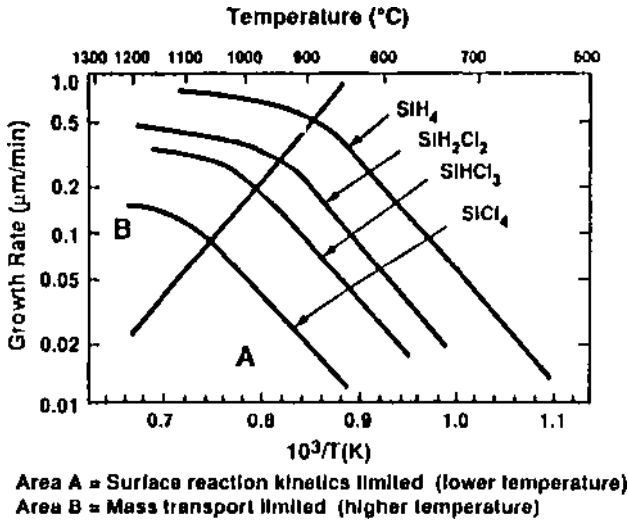


Figure 2.9. Arrhenius plot for silicon deposition using various precursors.

In the A sector (lower right), the deposition is controlled by surface-reaction kinetics as the rate-limiting step. In the B sector (upper left), the deposition is controlled by the mass-transport process and the growth rate is related linearly to the partial pressure of the silicon reactant in the carrier gas. Transition from one rate-control regime to the other is not sharp, but involves a transition zone where both are significant. The presence of a maximum in the curves in Area B would indicate the onset of gas-phase precipitation, where the substrate has become starved and the deposition rate decreased.

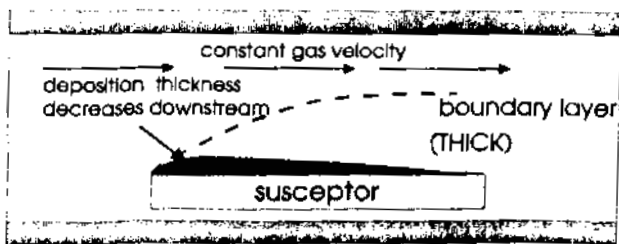
3.11 Pressure as Rate-Limiting Factor

Pressure is similar to temperature as a rate limiting factor since the diffusibility of a gas is inversely related to its pressure. For instance, lowering the pressure 760 Torr (1 atm) to 1 Torr increases the gas-phase transfer of reactants to the deposition surface and the

diffusion out of the by-products by more than 100 times. Clearly, at low pressure, the effect of mass-transfer variables is far less critical than at higher pressure.

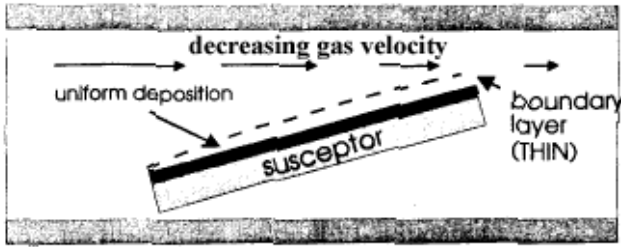
However, the gain may not be as large if the overall pressure decrease is at the expense of the partial pressure of reactant gas, since the kinetic rate (for first-order reactions) is proportional to the partial pressure of the reactant. Reducing the pressure by reducing the flow of carrier gas (or eliminating altogether) is a good alternative and is usually beneficial. At low pressure, surface reaction is the rate determining step and the mass-transfer variables are far less critical than at atmospheric pressure.

It can be now seen that, by proper manipulation of the process parameters and reactor geometry, it is possible to control the reaction and the deposition to a great degree. This is illustrated by the following example. In the deposition of tungsten in a tube mentioned in Sec. 3.2 above, the gas velocity is essentially constant and the boundary layer gradually increases in thickness toward downstream. This means that the thickness of the deposit will decrease as the distance from the tube inlet increases, as shown in Fig. 2.10a. This thickness decrease can be offset and a more constant thickness obtained simply by tilting the susceptor, as shown in Fig. 2.10b. This increases the gas velocity due the flow constriction; the Reynolds number goes up; the boundary layer decreases and the deposition rate is more uniform.^[14]



(a)

Figure 2.10. Control of deposition uniformity in a tubular reactor (a) susceptor parallel to gas flow, (b) tilted susceptor.



(b)

Figure 2.10. (*Cont'd.*)

3.12 Mathematical Expressions of the Kinetics of CVD

The flow-dynamics and mass-transport processes can be expressed mathematically and realistic models obtained to be used in the predictions of a CVD operation and in the design of reactors.^{[16]–[18]} These models are designed to define the complex entrance effects and convection phenomena that occur in a reactor and solve the complete equations of heat, mass balance, and momentum. They can be used to optimize the design parameters of a CVD reactor such as susceptor geometry, tilt angle, flow rates, and others. To obtain a complete and thorough analysis, these models should be complemented with experimental observations, such as the flow patterns mentioned above and in situ diagnostic, such as laser Raman spectroscopy.^[19]

4.0 GROWTH MECHANISM AND STRUCTURE OF DEPOSIT

In the previous sections, it was shown how thermodynamic and kinetic considerations govern a CVD reaction. In this section, the nature of the deposit, i.e., its microstructure and how it is controlled by the deposition conditions, is examined.

4.1 Deposition Mechanism and Epitaxy

The manner in which a film is formed on a surface by CVD is still a matter of controversy and several theories have been advanced to describe the phenomena.^[2] A thermodynamic theory proposes that a solid nucleus is formed from supersaturated vapor as a result of the difference between the surface free energy and the bulk free energy of the nucleus. Another and newer theory is based on atomistic nucleation and combines chemical bonding of solid surfaces and statistical mechanics.^[20] These theories are certainly valuable in themselves but considered outside the scope of this book.

There are, however, three important factors that control the nature and properties of the deposit to some degree which must be reviewed at this time: epitaxy, gas-phase precipitation, and thermal expansion.

4.2 Epitaxy

The nature of the deposit and the rate of nucleation at the very beginning of the deposition are affected, among other factors, by the nature of the substrate. A specific case is that of epitaxy where the structure of the substrate essentially controls the structure of the deposit.^{[2][15][20]} Epitaxy can be defined as the growth of a crystalline film on a crystalline substrate, with the substrate acting as a seed crystal. When both substrate and deposit are of the same material (for instance silicon on silicon) or when their crystalline structures (lattice parameters) are identical or close, the phenomena is known as homoepitaxy. When the lattice parameters are different, it is heteroepitaxy. Epitaxial growth cannot occur if these structural differences are too great.

A schematic of epitaxial growth is shown in Fig. 2.11. As an example, it is possible to grow gallium arsenide epitaxially on silicon since the lattice parameters of the two materials are similar. On the other hand, deposition of indium phosphide on silicon is not possible since the lattice mismatch is 8%, which is too high. A solution is to use an intermediate buffer layer of gallium arsenide between the silicon and the indium phosphide. The lattice parameters of common semiconductor materials are shown in Fig. 2.12.

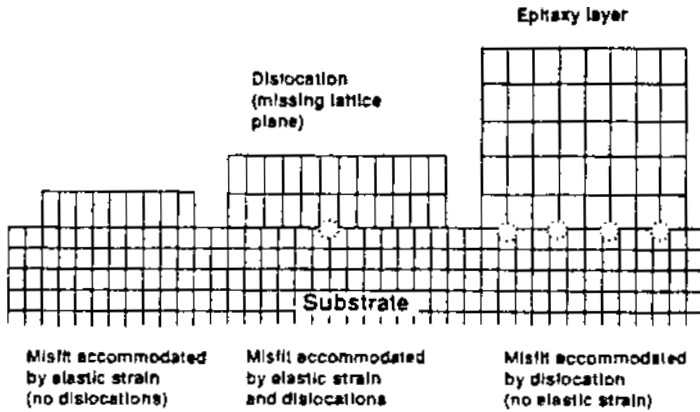


Figure 2.11. Epitaxy accommodations of lattice mismatch.

Generally, epitaxial films have superior properties and, whenever possible, epitaxial growth should be promoted. The epitaxial CVD of silicon and III–V and II–VI compounds is now a major process in the semiconductor industry and is expected to play an increasingly important part in improving the performance of semiconductor and optoelectronic designs (see Chs. 13–15).^[22]

4.3 Gas Phase Precipitation

As mentioned previously, a CVD reaction may occur in the gas phase instead of at the substrate surface if the supersaturation of the reactive gases and the temperature are sufficiently high. This is generally detrimental because gas-phase precipitated particles, in the form of soot, become incorporated in the deposit, causing nonuniformity in the structure, surface roughness, and poor adhesion. In some cases, gas-phase precipitation is used purposely, such as in the production of extremely fine powders (see Ch. 19).

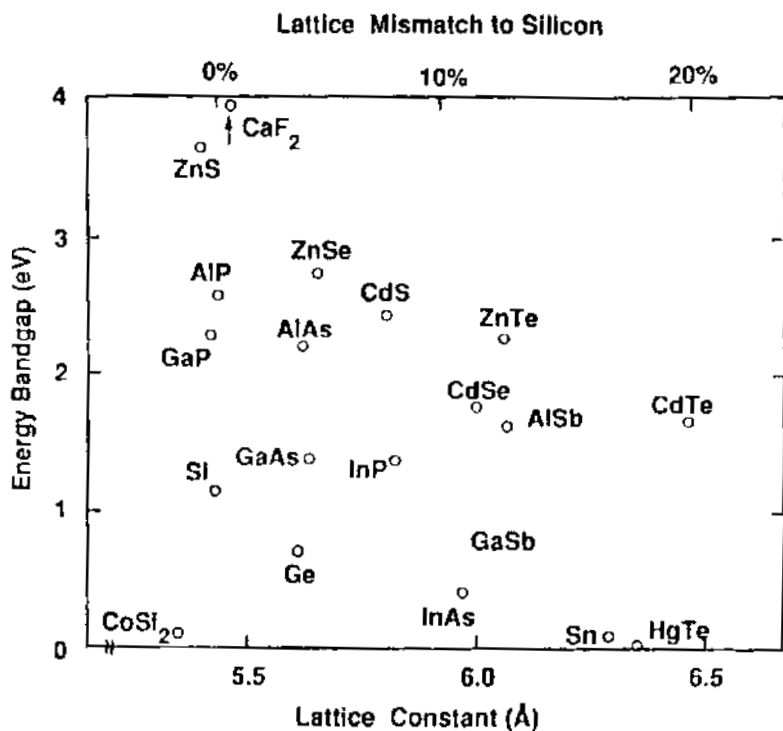


Figure 2.12. Bandgap and lattice constant of semiconductor materials.

4.4 Thermal Expansion

Large stresses can be generated in a CVD coating during the cooling period from deposition temperature to room temperature, if there is a substantial difference between the coefficient of thermal expansion (CTE) of the deposit and that of the substrate. These stresses may cause cracking and spalling of the coating. If differences are large, it may be necessary to use a buffer coating with an intermediate CTE or with high ductility. Deposition processes which

do not require high temperatures, such as MOCVD or plasma CVD, should also be considered (see Ch. 4 and 5). Table 2.1 lists the CTE of typical CVD materials and substrates.

4.5 Structure and Morphology of CVD Materials

The properties of a CVD material are directly related to the nature of its structure which is in turn controlled by the deposition conditions. In this section and the next, the relationship between properties, structure, and deposition conditions is examined.

The structure of a CVD material can be classified into three major types which are shown schematically in Fig. 2.13.^[23] In Zone (A), the structure consists of columnar grains which are capped by a domelike top. In Zone (B), the structure is also columnar but more faceted and angular. In Zone (C), it consists of fine accost grains. Examples of these structures are shown in Fig. 2.14.^[24] This is the CVD equivalent of the structural model for vacuum-evaporated films first introduced by Movchan and Demshishin.^[25]

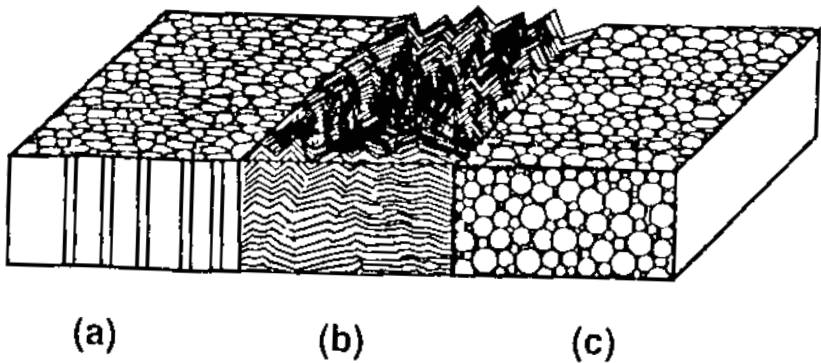
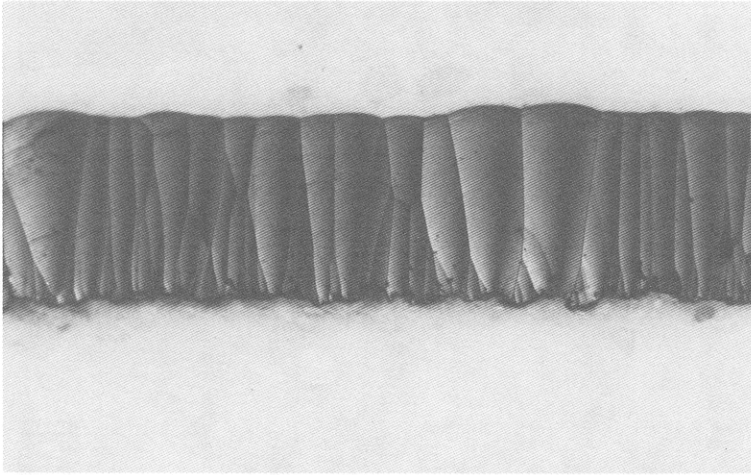


Figure 2.13. Schematic of structures obtained by CVD: (a) columnar grains with domed tops, (b) faceted columnar grains, (c) equiaxed fine grains.

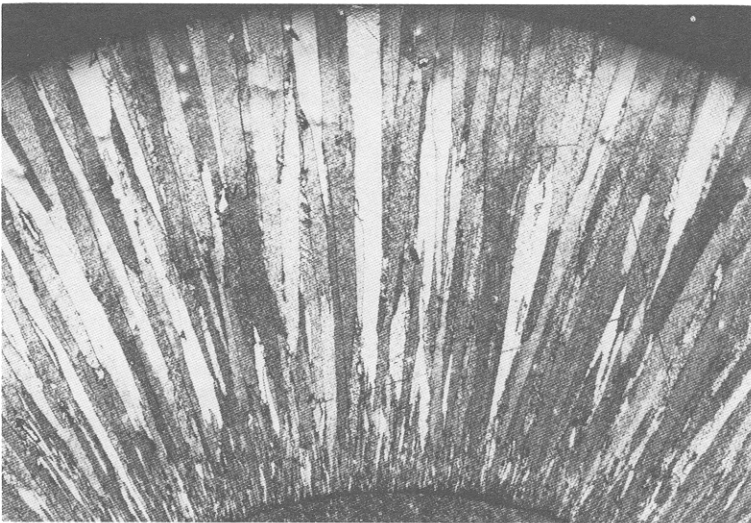
Table 2.1
Coefficient of Thermal Expansion (CTE) of Typical CVD Materials
and Substrates

Materials	CTE (ppm/°C) 25–300°C
Metals	
Aluminum	23.5
Gold	14.2
Iridium	6
Molybdenum	5
Niobium	7
Steel (carbon)	12
Stainless Steel (302)	17.3
Tantalum	6.5
Titanium	9
Tungsten	4.5
Non Metallic Elements	
Carbon, hot-pressed	5.4
Carbon-carbon	0.5
Silicon	3.8
Ceramics	
Alumina	8.3
Boron carbide	4.5
Boron nitride	7.5
Chromia	8
Hafnia	7
Magnesia	13
Molybdenum disilicide	8.25
Silicon carbide	3.9
Silicon nitride	2.45
Silicon oxide	0.5
Titanium carbide	7.6
Titanium diboride	6.6
Titanium nitride	9.5
Tungsten carbide	4.5
Tungsten disilicide	6.6

Note: Reported values of CTE's often vary widely. The values listed here are an average from several sources.

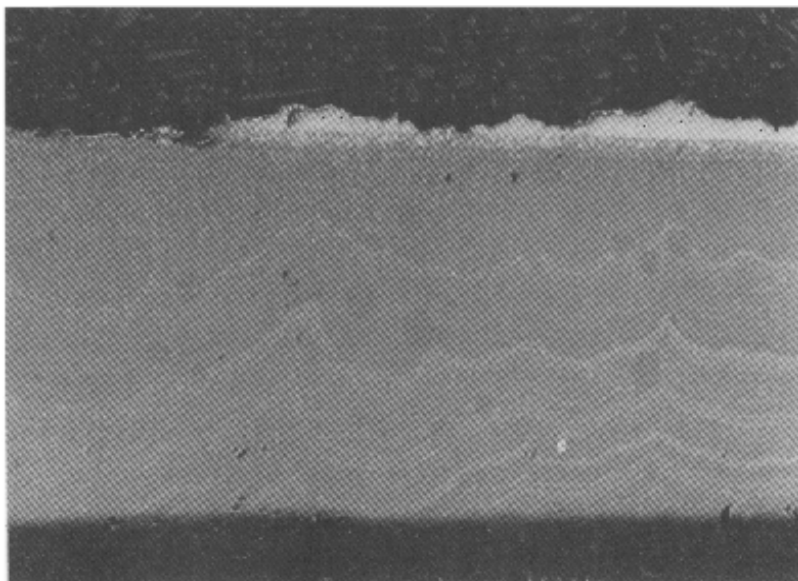


(a)

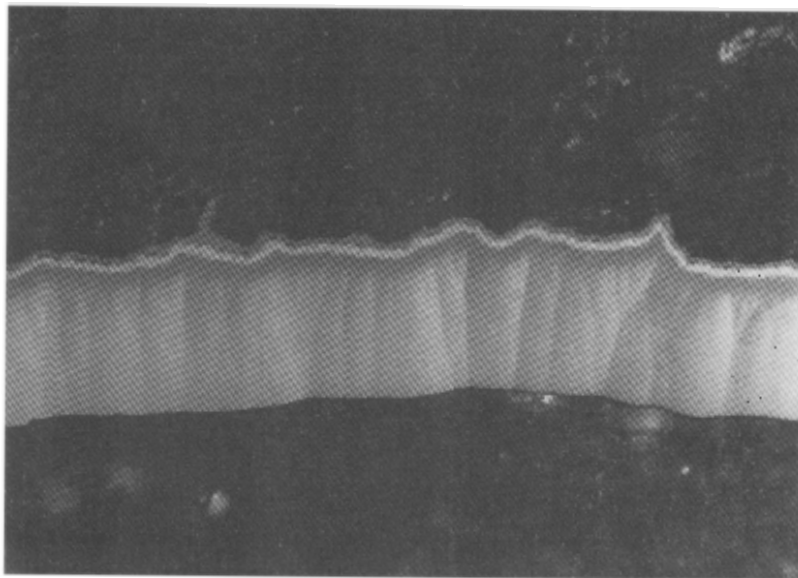


(b)

Figure 2.14. Examples of CVD structures: (a) columnar grains with domed tops, (b) faceted columnar grains, (c) equiaxed fine grains, (d) mixed structures. (Source: Ultramet, Pacoima, CA.)



(c)



(d)

Figure 2.14. (*Cont'd.*)

As might be expected, the microstructure varies depending on the material being deposited. In general, ceramics obtained by CVD such as SiO_2 , Al_2O_3 , Si_3N_4 , and most dielectric materials tend to be amorphous or, at least, have a very small grain microstructure (Type C). Metal deposits tend to be more crystalline with the typical columnar structure of type (A) or (B). The crystal size of the deposits is also a function of deposition conditions, especially temperature. Generally, the most desirable structure for load-bearing use is the fine accost (C), which usually has the highest mechanical properties, such as hardness and fracture toughness.

More often than not, a deposited structure will include two and sometimes all three types. This usually happens in thick deposits where a uniform structure is more difficult to obtain.

4.6 Control of CVD Microstructure

It is possible to control the nature of a CVD structure by the proper manipulation of the deposition parameters such as temperature, pressure, supersaturation, and the selection of the CVD reaction.

Pressure controls the thickness of the boundary layer and consequently the degree of diffusion as was shown above. By operating at low pressure, the diffusion process can be minimized and surface kinetics becomes rate controlling. Under these conditions, deposited structures tend to be fine-grained, which is usually a desirable condition (Fig. 2.13c). Fine-grained structures can also be obtained at low temperature and high supersaturation as well as low pressure.

At higher temperatures, deposits tend to be columnar (Fig. 2.13 a and b) as a result of uninterrupted grain growth toward the reactant source. The structure is also often dependent on the thickness of the deposit. For instance, grain size will increase as the thickness increases. A columnar-grain structure develops, which becomes more pronounced as the film becomes thicker.

Columnar structures are usually undesirable as the deleterious effects of grain growth and columnar formation can be considerable. They may lead to structural, chemical, and electrical anisotropy and the rapid diffusion of impurities along the grain boundaries. It is possible to reduce or eliminate columnar deposits and obtain fine-grain accost growth by mechanical means such as rubbing or brushing at regular intervals to renucleate the deposition surface. This approach has been demonstrated in the deposition of tungsten.^[13] However, it is not generally practical, particularly when substrates of complex geometry are used.

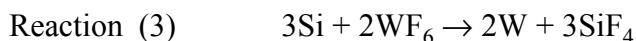
Another approach is the control of grain growth by chemical means.^{[26][27]} In the deposition of tungsten for instance, a fine-grain equiaxial growth is obtained by depositing alternating layers of tungsten and silicon. Typically a layer of tungsten, approximately 100 nm thick, is deposited using the hydrogen reduction of WF_6 at 550°C and a pressure of a few Torr as follows:



A 15 nm thick layer of silicon is then deposited by the thermal decomposition of silane at the same temperature and pressure as follows:



WF_6 is then reintroduced in the system and the thin layer of silicon is reduced as follows:



After the silicon is completely reduced, Reaction (3) stops and Reaction (1) is resumed. The temporary deposition of sacrificial silicon interrupts the tungsten grain growth as new nucleation sites are created. Larger grain and columnar growth are essentially eliminated

and a fine-grain structure is the result. A similar process can be used for the deposition of rhenium and other metals.

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3

The Chemistry of CVD

1.0 CATEGORIES OF CVD REACTIONS

Before any CVD program is undertaken, it is essential to evaluate all the potential reactions and select the most appropriate. This is done by a thermodynamic analysis as described in Ch. 2 and, if necessary, by an experimental program.

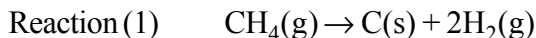
The CVD reactions can be classified in several major categories which are outlined below. These reactions and others are described in greater detail in Chs. 6–11 where the materials produced by CVD are reviewed.

Metallo-organic CVD (MOCVD) is major area of CVD which is rapidly growing, particularly in semiconductor and optoelectronic applications. It is treated separately in Ch. 4.

1.1 Thermal-Decomposition (or Pyrolysis) Reactions

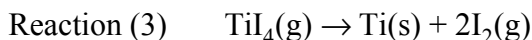
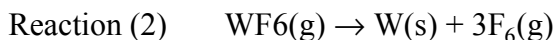
In thermal-decomposition reactions, a molecule is split into its elements and/or a more elementary molecule. Such reactions are the simplest since only one precursor gas is required. Typical examples are as follows:

Hydrocarbon Decomposition

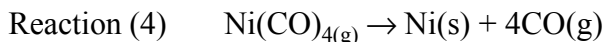


This reaction is used extensively in the production of carbon, graphite and diamond.

Halide Decomposition (See Sec. 3 Below)

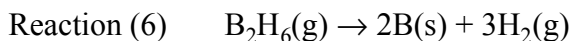
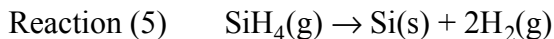


Carbonyl Decomposition (See Sec. 4 Below)



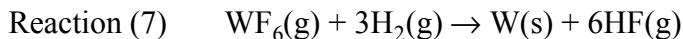
This also includes the decomposition of the more complex carbonyls such as the carbonyl hydrides and nitrosylcarbonyls.

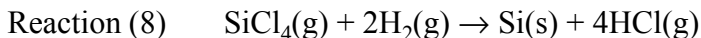
Hydride Decomposition (See Sec. 5 Below)



1.2 Hydrogen Reduction

Reduction is a chemical reaction in which an element gains an electron, in other words, when the oxidation state is lowered.^[1] Reduction reactions are widely used, particularly the hydrogen reduction of the halides, as shown in the following examples:





These two reactions are actually simplified versions and several intermediate reactions generally occur with the formation of lower halides.

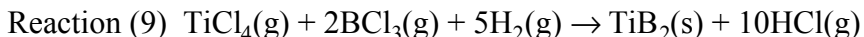
Hydrogen reduction has a major advantage in that the reaction generally takes place at lower temperature than the equivalent decomposition reaction. It is used extensively in the deposition of transition metals from their halides, particularly the metals of Groups Va, (vanadium, niobium, and tantalum) and VIa (chromium, molybdenum, and tungsten). The halide reduction of Group IVa metals (titanium, zirconium, and hafnium) is more difficult because their halides are more stable.

The hydrogen reduction of the halides of nonmetallic elements, such as silicon (Reaction 8) and boron, is an essential process in the production of semiconductors and high-strength fibers.

Note: Hydrogen is used in a supplementary role in reactions where reduction is not the primary function, for instance where it is necessary to prevent the formation of oxides or carbides and generally improve the characteristics and properties of the deposited material.

1.3 Coreduction

The deposition of a binary compound can be achieved by a coreduction reaction. In this manner, ceramic materials such as oxides, carbides, nitrides, borides, and silicides can be produced readily and usually more readily than the parent metal. A common example is the deposition of titanium diboride:



1.4 Metal Reduction of the Halides

Although hydrogen is the most common reductant, there are other elements which are more powerful, such as zinc, cadmium, magnesium, sodium, and potassium, as shown in Table 3.1.

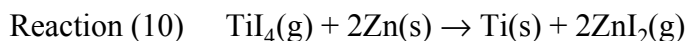
Table 3.1

Free Energy of Formation of Reductant Elements^[2]

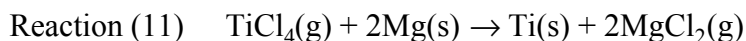
Reduc- tant	Melt Point °C	Boil Point °C	Chloride	Standard Free Energy of Formation (KJoule per mole) at the given temperatures (°C)			
				425	725	1025	1325
H ₂			HCl	-98	-100	-102	-104
Cd	320	765	CdCl ₂	-264	-241	-192	-164
Zn	419	906	ZnCl ₂	-307	-264	-262	-254
Mg	650	1107	MgCl ₂	-528	-482	-435	-368
Na	97	892	NaCl	-223	-238	-241	229
K	631	760	KCl	-369	-341	-295	

In this table, the free energy of formation, ΔG_f° , of the chloride of these metals is listed for four different temperatures. As can be seen, the values are more negative than that of hydrogen chloride. These metals can be used to reduce the halides of titanium, zirconium, or hafnium, whereas hydrogen, as mentioned above, cannot do so readily. In order to be useful in CVD, the by-product chloride must be volatile at the deposition temperature. This may rule out the use of sodium or potassium, which evaporate above 1400°C.

Of these reductant metals, the most commonly used is zinc. The reason is that the zinc halides are more volatile than the parent metal and the chances of codeposition of the halides are minimized. Either chloride or iodide is used, although the iodide, being the most volatile, is usually preferred. The volatility of these halides decreases as one goes from the iodides to the chlorides to the fluorides. The reaction is as follows:



Another reductant, magnesium, is used in the industrial production of titanium metal as follows:

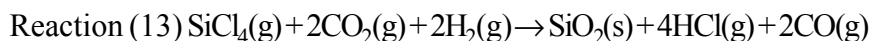
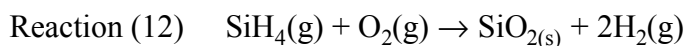


The alkali metals, sodium and potassium, shown in Table 3.1 are not generally used as reductant because their reductive power is so high that it tends to cause premature and detrimental gas-phase precipitation and, as mentioned above, high temperature is necessary to volatilize these metals.

1.5 Oxidation and Hydrolysis Reactions

Oxidation and hydrolysis are two important groups of CVD reactions which are used in the formation of oxides. Common sources of oxygen are the element itself and CO_2 . Recently, ozone (O_3) has been used for the deposition of SiO_2 .^{[3][4]} It is a powerful oxidizing agent which is often generated *in situ*, by a corona discharge in oxygen.

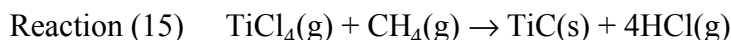
Typical oxidation and hydrolysis reactions are:





1.6 Carbidization and Nitridation

The deposition of carbides (carbidization) is usually obtained by reacting a halide with a hydrocarbon, such as methane, as follows:



The deposition of nitrides (nitridation or ammonolysis) is generally based on ammonia which is preferred to nitrogen. Ammonia has a positive free energy of formation; thus its equilibrium products are essentially hydrogen and nitrogen which become the reactants for the CVD reaction. The observed advantage of ammonia as a reactant lies in the kinetics of the nascent hydrogen and nitrogen atoms from the ammonia decomposition. Thermodynamically, the reaction of 2NH_3 and of N_2 and H_2 are equivalent.

An example of the use of ammonia is the deposition of silicon nitride, a common reaction in the semiconductor industry:^[5]



2.0 CVD PRECURSORS

In the previous section, the general categories of CVD reactions were reviewed and, as can be readily seen, the choice of the proper reactants (the precursors) is very important. These precursors fall into several general groups which are the halides, carbonyls and hydrides (the metallo-organics are reviewed in Ch. 4). A general review of the nature and properties of these precursors is given in this section which should help in making the proper precursor selection and gaining a better understanding of the CVD reactions.

The choice of a precursor is governed by certain general characteristics which can be summarized as follows:

- Stability at room temperature.
- Ability to react cleanly in the reaction zone.
- Sufficient volatility at low temperature so that it can be easily transported to the reaction zone without condensing in the lines.
- Capability of being produced in a very high degree of purity.
- Ability to react without producing side reactions or parasitic reactions.

3.0 HALIDE PRECURSORS

The halides are binary compounds of a halogen (elements of group VIIb of the periodic table) and a more electropositive element such as a metal.

3.1 Halogens

The halogens include fluorine, chlorine, bromine and iodine and all have been used in CVD reactions. They are reactive elements and exist as diatomic molecules, i.e., F_2 , Cl_2 , etc. Their relevant properties are listed in Table 3.2.

Of all the elements, fluorine is the most chemically reactive. It combines directly with other elements. Chlorine is slightly less reactive. Both are gases at room temperature which is an important advantage in delivery and metering. Because of their reactivity, they form halides readily, but also attack most materials which makes them difficult to handle and requires equipment designed with inert materials such as Monel or Teflon. Halogens are also toxic, fluorine more so than chlorine by an order of magnitude.

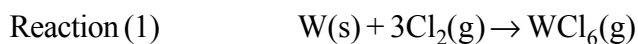
Table 3.2
Relevant Properties of the Halogens^[6]

Element	Electron Affinity KJ g-atom	Boiling Point °C	Melting Point °C
Fluorine	339	-118	-233
Chlorine	355	-34.6	-103
Bromine	331	58.7	-7.2
Iodine	302	184.3	113.5

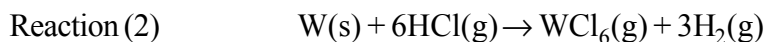
Bromine is a dark-red liquid with high specific gravity. Iodine is a black solid which sublimates at atmospheric pressure producing a violet vapor. Both are used in CVD but to a lesser degree than either fluorine or chlorine.

3.2 Halide Formation or Halogenation

Halides can be formed by the direct interaction of the halogen as follows:



or by the reaction with another halide such as hydrogen chloride:



Reaction (2) is often preferred because of the hazard of unconsumed chlorine from Reaction (1) reacting explosively with hydrogen commonly used as a reducing agent.

3.3 Halide Properties

Properties of some halides useful in CVD are listed in Table 3.3. As can be seen, some of these halides are gaseous or liquid at room temperature and, as such, are easily transported in the reaction chamber. The solid halides, however, must be heated to produce sufficient vapor. This sometimes presents a problem which can be bypassed by generating the halide *in situ* (see Ch. 5). Most halides are available commercially.

Table 3.3
Properties of Selected Halides^[6]

Halides	Melting Point °C	Boiling Point °C
AlBr ₃	97.5	263
AlCl ₃	190	182.7 (s)
BCl ₃	-107.3	12.5
BF ₃	126.7	-99.9
CCl ₄	-23	76.8
CF ₄	-184	-128
CrCl ₂	824	1300 (s)
HfCl ₄	319	319 (s)
HfI ₄		400 (s)
MoCl ₅	194	268
MoF ₆	17.5	35
NbCl ₅	204.7	254
ReF ₆	18.8	47.6
SiCl ₄	-70	57.6
TaBr ₅	265	348.8
TaCl ₅	216	242
TiCl ₄	-25	136
VCl ₄	-28	148.5
WCl ₅	248	275.6
WF ₆	2.5	17.5
ZrBr ₄	450	357 (s)
ZrCl ₄	437	331 (s)
<i>Note:</i> (s) indicates that the compound sublimes at atmospheric pressure before melting.		

4.0 METAL-CARBONYL PRECURSORS

Metal carbonyls form a large and important group of compounds which are used widely in the chemical industry, particularly in the preparation of heterogeneous catalysts and as precursors in CVD and metallo-organic CVD (MOCVD).

4.1 Characteristics of the Carbonyls

The carbonyls are relatively simple compounds since they consist of only two components:

- The carbonyl group which is a functional group where a carbon atom is doubly bonded to an oxygen atom(CO) .
- A d-group transition metal.

The atomic structure of the transition metals is such that the *d* shell is only partly filled. The first transition series (3d) comprises Sc, Ti, V, Cr, Mn, Fe, Co, and Ni; the second (4d), Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, and Ag; the third (5d), Hf, Ta, W, Re, Os, Ir, Pt, and Au. Carbonyl derivatives of at least one type are found for all these metals. Although only a few are presently used in CVD, many are being investigated as they constitute an interesting and potentially valuable group of precursor materials.

The simplest transition metal carbonyls are mononuclear of the type $M(CO)_x$, in other words those with only one metal atom. They are hydrophobic but soluble to some extent in nonpolar liquids, such as n-butane or propane. The dinuclear carbonyls are more complex but have the same general characteristics as the mononuclear carbonyls. The carbonyls, which are or could be used in CVD, are listed in Table 3.4 with some of their properties.

More complex yet are the polynuclear or cluster carbonyls, some of which are used as CVD precursors such as: $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, and $Ir_4(CO)_{12}$.

Table 3.4
Selected Properties of Metal Carbonyls^{[1][7]}

Compound	MP °C	BP °C	Sp.Gr.	Color & Form	Structure	Comments
MONONUCLEAR						
V(CO) ₆	65	dec.		Black crystal	Octahedral	Yellow-orange in solution, volatile, very unstable
Cr(CO) ₆	164	dec. 180	1.77	White crystal	Octahedral	Volatile
Fe(CO) ₅	-20	103	1.42	Yellow liquid		Poisonous
Ni(CO) ₄	-25	43	1.32	Colorless liquid		Very toxic
Mo(CO) ₆	150	dec. 180		White crystal	Octahedral	Volatile
Ru(CO) ₅	-22			Colorless liquid		Very volatile
W(CO) ₆	169	dec. 180	2.65	White crystal	Octahedral	Volatile
Os(CO) ₅	-15			Colorless liquid		Very volatile
DINUCLEAR						
Mn ₂ (CO) ₁₀	152			Crystal		
Fe ₂ (CO) ₉	80 dec.	2.08		Yellow crystal	Hexagonal	Volatile
Co ₂ (CO) ₈	51	52 dec.	1.73	Orange crystal		CO loss
Re ₂ (CO) ₁₀	170	250 dec.		Colorless crystal		Cubic Volatile
Ir ₂ (CO) ₈	160			Yellow crystal		Sublimes in CO ₂ at 160°C

4.2 Carbonyl Preparation

Many metal carbonyls are available commercially. However, in some cases, the CVD investigator may find it more expedient (and sometimes cheaper) to produce them in-house. This is particularly true of the only two carbonyls that can be obtained by the direct reaction of the metal with CO (and consequently easy to synthesize), i.e., nickel carbonyl, $\text{Ni}(\text{CO})_4$, and iron carbonyl, $\text{Fe}(\text{CO})_5$.

Table 3.5 summarizes the various synthesis processes.

Table 3.5
Metal Carbonyl Preparation

Carbonyl	Process
$\text{Ni}(\text{CO})_4$	Direct reaction with CO at one atm and at 80°C
$\text{Fe}(\text{CO})_5$	Direct reaction with CO at one atm and at 150–300°C
$\text{Co}_2(\text{CO})_8$	Reaction of the carbonate with CO at 250–300 atm and at 120–200°C
$\text{V}(\text{CO})_6$ $\text{Cr}(\text{CO})_6$ $\text{W}(\text{CO})_6$ $\text{Re}_2(\text{CO})_{10}$	Reaction of the chloride with CO with a reducing agent at 200–300 atm and at 300°C
$\text{Os}(\text{CO})_5$ $\text{Re}_2(\text{CO})_{10}$	Reaction of the oxide with CO at 300°C
$\text{Ru}_3(\text{CO})_{12}$	Reaction of acetylacetonate with CO at 150°C and 200 atm

4.3 Metal Carbonyl Complexes

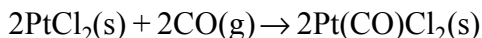
Metal carbonyls form several complexes but those of major interest in MOCVD are the carbonyl halides and the carbonyl-nitric-oxide complexes.

The carbonyl halides have the general formula $M_x(CO)_yX_z$ with X being fluorine, chlorine, bromine, or iodine. With the notable exception of nickel, most metals form carbonyl halides including all the metals listed in Table 3.4.

A particularly interesting case is that of the platinum metal group which, in addition to platinum (Pt), comprises ruthenium (Ru), osmium (Os), rhodium (Rh), iridium (Ir), and palladium (Pd). These carbonyl halides are usually the most practical precursors for metal deposition because of their high volatility at low temperature. Indeed two of them, palladium and platinum, do not form carbonyls but only carbonyl halides. So does gold.

The hydrogen reduction of the metal halides, described in Sec. 1.2, is generally the favored reaction for metal deposition but is not suitable for the platinum-group metals since the volatilization and decomposition temperatures of their halides are too close to provide efficient vapor transport.^[2] For that reason, the decomposition of the carbonyl halide is preferred. The exception is palladium which is much more readily deposited by hydrogen reduction than by the carbonyl-halide decomposition.

Preparation of Carbonyl Halides. The carbonyl halides are generally produced by the direct reaction of the metal halide and CO, usually at high pressure and at the temperature range of 140–290°C. A typical reaction is:^[8]



Some examples of carbonyl halides are shown in Table 3.6.

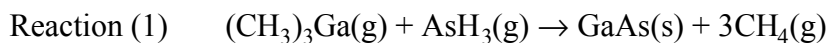
Carbonyl Nitric Oxides. Another group of metal-carbonyl complexes, worthy of investigation as CVD precursors, consists of the carbonyl nitric oxides. In these complexes, one (or more) CO group is replaced by NO. An example is cobalt nitrosyl tricarbonyl, $CoNO(CO)_3$, which is a preferred precursor for the CVD of cobalt. It is a liquid with a boiling point of 78.6°C which decomposes at 66°C. It is prepared by passing NO through an aqueous solution of cobalt nitrate and potassium cyanide and potassium hydroxide.^[9]

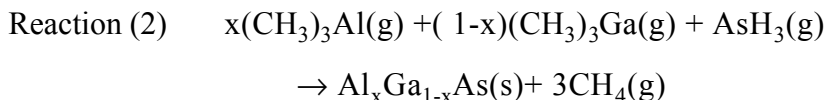
Table 3.6
Metal Carbonyl Halides^[1]

Compound	MP°C	BP°C	Sp.Gr.	Color & Form	Comments
Mn(CO) ₅ Cl				Yellow crystal	Loses CO at 120°C in organic solvent
Re(CO) ₄ Cl ₂		250 dec.		White crystal	
Ru(CO) ₂ I ₂				Orange powder	Suitable for CVD
Os(CO) ₃ Cl ₂	270	280 dec.		Colorless prism	Suitable for CVD
RhCl ₂ RhO(CO) ₃	125	subl.		Ruby red needle cr.	Suitable for CVD
Ir(CO) ₂ Cl ₂	140 dec.			Colorless needle cr.	Suitable for CVD
Pt(CO)Cl ₂	195	300 dec.	4.23	Yellow needle cr.	Sublimes in CO ₂ at 240°C Suitable for CVD
Pt(CO) ₂ Cl ₂	142	210	3.48	Light yel. needle cr.	Sublimes in CO ₂ at 210°C

5.0 HYDRIDE PRECURSORS

Hydrides are an important group of precursors that are used to deposit single elements such as boron or silicon. As described in Ch. 4, they are also used in conjunction with metallo-organics to form III–V and II–VI semiconductor compounds as shown in the following examples:^[10]





Many elements form hydrides but only few hydrides are presently used as CVD precursors. These are the hydrides of elements of groups IIIb, IVb, Vb, and VIb, which are all covalent. They are listed in Table 3.7.

Table 3.7
Hydrides Used in CVD (Partial List)^{[1][6]}

Element	Name	Formula	Boiling Point °C
As	Arsine	AsH ₃	-55
B	Diborane	B ₂ H ₆	-92
Ge	Germane	GeH ₄	-88
N	Ammonia	NH ₃	-33
P	Phosphine	PH ₃	-87
S	Hydrogen sulfide	H ₂ S	-60
Sb	Stibine	SbH ₃	-17
Se	Hydrogen selenide	H ₂ Se	3
Si	Silane	SiH ₄	-111
Te	Hydrogen telluride	H ₂ Te	-2

Note: Most of these compounds are extremely toxic. Manufacturer's recommendations must be carefully followed.

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4

Metallo-Organic CVD (MOCVD)

1.0 INTRODUCTION

Metallo-organic CVD (MOCVD) is a specialized area of CVD, which is a relatively newcomer, as its first reported use was in the 1960s for the deposition of indium phosphide and indium antimonide. These early experiments demonstrated that deposition of critical semiconductor materials could be obtained at lower temperature than conventional thermal CVD and that epitaxial growth could be successfully achieved. The quality and complexity of the equipment and the diversity and purity of the precursor chemicals have steadily improved since then and MOCVD is now used on a large scale, particularly in semiconductor and opto-electronic applications.^{[1][2]}

Metallo-organics are compounds in which the atom of an element is bound to one or more carbon atoms of an organic hydrocarbon group. Many of the elements used in MOCVD are the metals of groups IIa, IIb, IIIb, IVb, Vb, and VIb, which are non-transitional. The metallo-organics thus complement the halides and carbonyls, which are the precursors for the deposition of transition metals (Groups IVa, Va, and VIa) and their compounds.

The term *metallo-organic* is used somewhat loosely in CVD parlance, since it includes compounds of elements, such as silicon, phosphorus, arsenic, selenium, and tellurium, that are not considered metallic. To conform to what appears to be a well-established tradition, such nonmetal compounds will be included here as metallo-organics.

2.0 MOCVD PROCESS AND EQUIPMENT

Most MOCVD reactions occur in the temperature range of 300–800°C and at pressure varying from less than 1 Torr to atmospheric. A typical reactor for the deposition of the optoelectronic material gallium-aluminum-arsenide (GaAlAs) is shown in Fig. 4.1. Because of the highly critical requirements of most semiconductor applications, it is necessary to use the most accurate controls and high-purity reactants. Electronic mass-flow controllers, ultrafast bellows-sealed gas-switching valves, accurate venting controls, and complete elimination of dead space allow rapid switching of gases. As a result, deposits of less than 10 nm in thickness and with abrupt interfaces of less than 1 nm can be produced.^[3]

The equipment and chemicals used in MOCVD are all available commercially but are expensive and production cost is high. For these reasons, MOCVD is considered in applications where high quality is essential.

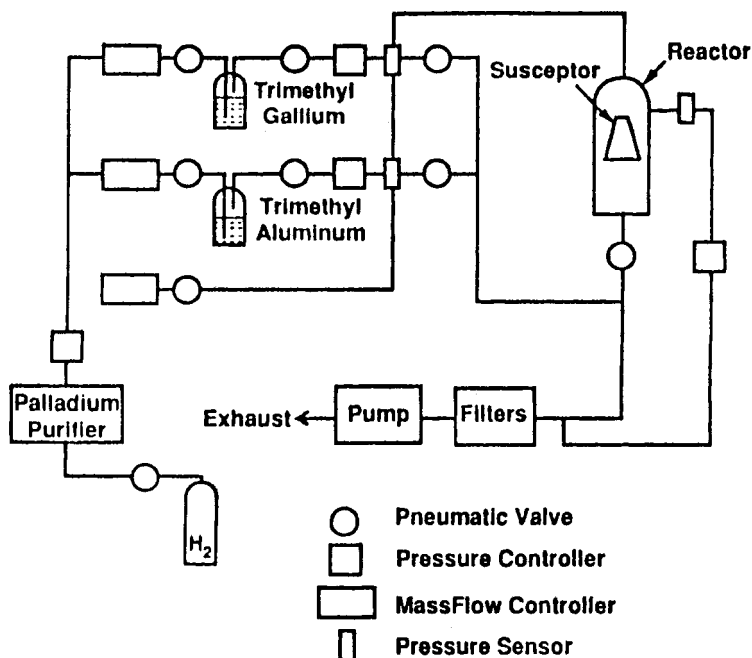


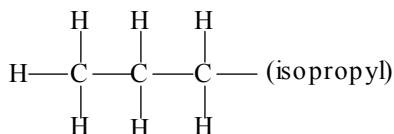
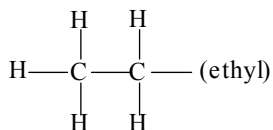
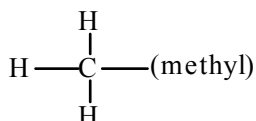
Figure 4.1. Schematic of typical MOCVD system.

3.0 MOCVD PRECURSORS: ALKYL, ALICYCLIC, AND ARYL COMPOUNDS

In the following sections, the major categories of metallo-organic compounds used in CVD are reviewed. Others are described in the review of materials produced by CVD in Chs. 6–12. These metallo-organics form only a small proportion of the total number of compounds available and there are many that could be profitably investigated.

3.1 Alkyls

A major MOCVD group is that of the alkyls. These are formed by reacting an aliphatic hydrocarbon or an alkyl halide with a metal.^[4] These hydrocarbons are composed of chains of carbon atoms as shown below:^[5]

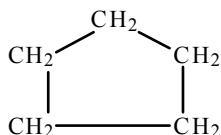


These alkyls are nonpolar volatile liquids. The methyl metallo-organics start to decompose at 200°C and the ethyl metallo-organics at approximately 110°C.

3.2 Alicyclic Compounds

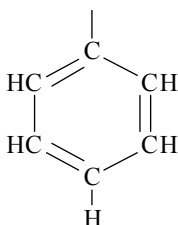
Other common MOCVD compounds are produced from alicyclic hydrocarbons, where the carbon chain forms a ring, such as in

cyclopentane shown below:



3.3 Aryl Compounds

Other MOCVD compounds are the aryls, which are formed from aromatic hydrocarbons, that is compounds that have six-member rings with three carbon double bonds, such as phenyl shown below:



Common metallo-organic alkyls, alicyclic, and aryl compounds and their relevant properties are listed in Table 4.1.^[6] Many additional organometallic compounds are available commercially as listed in Ref. 7.

Most metallo-organic compounds are monomers with some important exceptions, such as trimethyl aluminum which is a dimer. Their vapor pressures are usually directly related to the molecular weight, with the lower molecular weight compounds having the higher volatility.

To be useful as CVD precursors, a metallo-organic compound should be stable at room temperature so that its storage and transfer are not a problem. It should also decompose readily at low temperature, i.e., below 500°C. The compounds listed in Table 4.1 meet these conditions with the exception of the alkyls of arsenic and phosphorus, which decompose at higher temperatures. For that reason, the hydrides of arsenic and phosphorus are often preferred as CVD precursors (see Ch. 3). These hydrides however are extremely toxic and environmental considerations may restrict their use.

Table 4.1
Alkyls, Alicyclic, and Aryl Metallo-Organic Compounds

Compound	Formula	Type	MP°C	BP°C	Vapor Pressure mm
Trimethyl aluminum	(CH ₃) ₃ Al	Alkyl	15	126	8.4 @0°C
Triethyl aluminum	(C ₂ H ₅) ₃ Al	Alkyl	-58	194	
Triisobutyl aluminum	(C ₄ H ₉) ₃ Al	Alkyl	4	130	
Diisobutyl aluminum hydride	(C ₄ H ₉) ₂ AlH	Alkyl	-70	118	
Trimethyl arsenic	(CH ₃) ₃ As	Alkyl			238 @20°C
Diethyl arsine	(C ₂ H ₅) ₂ AsH ₂	Alkyl			0.8 @8°C
Diethyl beryllium	(C ₂ H ₅) ₂ Be	Alkyl	12	194	
Diphenyl beryllium	(C ₆ H ₅) ₂ Be	Aryl			
Dimethyl cadmium	(CH ₃) ₂ Cd	Alkyl	4	105	28 @20°C
Heptane dionato cesium	(TMHD) ₄ Ce	Alkyl	250(dec.)		0.05 @130
Trimethyl gallium	(CH ₃) ₃ Ga	Alkyl	-15	5	64 @0°C
Triethyl gallium	(C ₂ H ₅) ₃ Ga	Alkyl	-82	143	18 @48°C
Dimethyl mercury	(CH ₃) ₂ Hg	Alkyl	96		
Cyclopentadienyl mercury	(C ₅ H ₅) ₂ Hg	Cyclic			
Trimethyl indium	(CH ₃) ₃ In	Alkyl	88	134	1.7 @20°C
Triethyl indium	(C ₂ H ₅) ₃ In	Alkyl	-32	184	3 @53°C
Diethyl magnesium	(C ₂ H ₅) ₂ Mg	Alkyl			
Cyclopentadienyl magnesium	(C ₅ H ₅) ₂ Mg	Cyclic	176		
Ter-butyl phosphine	(C ₄ H ₉)PH ₂	Alkyl			285 @23°C
Triethyl phosphorus	(C ₂ H ₅) ₃ P	Alkyl			10.8 @20°C
Tetramethyl lead	(CH ₃) ₄ Pb	Alkyl			
Tetraethyl lead	(C ₂ H ₅) ₄ Pb	Alkyl			

(Cont'd)

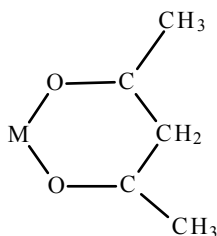
Table 4.1 (Cont'd)

Compound	Formula	Type	MP°C	BP°C	Vapor Pressure mm
Diethyl sulfur	(C ₂ H ₅) ₂ S	Alkyl			
Trimethyl antimony	(CH ₃) ₃ Sb	Alkyl			
Trimethyl tin	(CH ₃) ₃ Sn	Alkyl			
Cyclopentadienyl tin	(C ₅ H ₅) ₂ Sn	Cyclic			
Diethyl telluride	(C ₂ H ₅) ₂ Te	Alkyl			7@20°C
Terakis dimethylamine titanium	[N(CH ₃) ₂] ₄	Alkyl			
Dimethyl zinc	(CH ₃) ₂ Zn	Alkyl	-42	46	124@0°C
Diethyl zinc	(C ₂ H ₅) ₂ Z	Alkyl	-28	118	6.4@20°C

Note: Most of these compounds are extremely reactive, especially the lower alkyls. Most of them are volatile, pyrophoric and in some cases react explosively on contact with water. Some are toxic. Manufacturer's recommendations must be carefully studied before use.

4.0 ACETYLACETONATE COMPOUNDS

Metal acetylacetonates (M-ac.ac), also known as pentanedionates, are produced by reacting metals and acetylacetone. They have the following chemical structure:



The acetylacetonates are stable in air and readily soluble in organic solvents. From this standpoint, they have the advantage over the alkyls and other alkoxides, which, with the exception of the iron alkoxides, are not as easily soluble. They can be readily synthesized in the laboratory. Many are used extensively as catalysts and are readily available. They are also used in CVD in the deposition of metals such as iridium, scandium and rhenium and of compounds, such as the yttrium-barium-copper oxide complexes, used as superconductors.^{[8][9]} Commercially available acetyl-acetonates are shown in Table 4.2.

Also increasingly common, as CVD precursors, are many halogen-acetylacetonate complexes, such as trifluoro-acetylacetonate thorium, $\text{Th}(\text{C}_5\text{H}_4\text{F}_3\text{O}_2)_4$, used in the deposition of thoriated tungsten for thermionic emitters,^[10] the trifluoro-acetylacetonates of hafnium and zirconium and the hexafluoro-acetylacetonates of calcium, copper, magnesium, palladium, strontium, and yttrium.

5.0 MOCVD REACTIONS FOR THE DEPOSITION OF METALS

Most metals can be deposited by MOCVD and in some cases the process is an important industrial operation. The metals most readily deposited by MOCVD are the non-transition metals. The following is a summary of the metallo-organic precursors and deposition condition presently used in development or production.

Table 4.2
Acetyl-Acetonates Organo-Metallic Compounds

Metal	Formula	Form	Melting Point °C
Barium	Ba(C ₅ H ₇ O ₂) ₂	Crystal	>320
Beryllium	Be(C ₅ H ₇ O ₂) ₂	White crystal	108
Calcium	Ca(C ₅ H ₇ O ₂) ₂	White crystal	175 dec.
Cerium	Ce(C ₅ H ₇ O ₂) ₃	Yellow crystal	131
Chromium	Cr(C ₅ H ₇ O ₂) ₃	Violet crystal	214
Cobalt	Co(C ₅ H ₇ O ₂) ₃	Green powder	240
Copper	Cu(C ₅ H ₇ O ₂) ₂	Blue crystal	230 (s)
Dysprosium	Dy(C ₅ H ₇ O ₂) ₃	Powder	
Erbium	Er(C ₅ H ₇ O ₂) ₃	Powder	
Gadolinium	Gd(C ₅ H ₇ O ₂) ₃	Powder	143
Indium	In(C ₅ H ₇ O ₂) ₃	Cream powder	186
Iridium	Ir(C ₅ H ₇ O ₂) ₃	Orange crystal	
Iron	Fe(C ₅ H ₇ O ₂) ₃	Orange powder	179
Lanthanum	La(C ₅ H ₇ O ₂) ₃	Powder	
Lead	Pb(C ₅ H ₇ O ₂) ₂	Crystal	
Lithium	LiC ₅ H ₇ O ₂	Crystal	ca 250
Lutetium	Lu(C ₅ H ₇ O ₂) ₃	Powder	
Magnesium	Mg(C ₅ H ₇ O ₂) ₂	Powder	dec.
Manganese	Mn(C ₅ H ₇ O ₂) ₂	Buff crystal	180
Neodymium	Nd(C ₅ H ₇ O ₂) ₃	Pink powder	150
Nickel	Ni(C ₅ H ₇ O ₂) ₂	Powder	238
Palladium	Pd(C ₅ H ₇ O ₂) ₂	Orange needle	210
Platinum	Pt(C ₅ H ₇ O ₂) ₂	Yellow needle	
Praseodymium	Pr(C ₅ H ₇ O ₂) ₃	Powder	
Rhodium	Rh(C ₅ H ₇ O ₂) ₃	Yellow crystal	
Samarium	Sm(C ₅ H ₇ O ₂) ₃	Powder	146
Scandium	Sc(C ₅ H ₇ O ₂) ₃	Powder	187
Silver	AgC ₅ H ₇ O ₂	Crystal	
Strontium	Sr(C ₅ H ₇ O ₂) ₂	Crystal	220
Terbium	Tb(C ₅ H ₇ O ₂) ₃	Powder	
Thorium	Th(C ₅ H ₇ O ₂) ₄	Crystal	171 (s)
Thulium	Tm(C ₅ H ₇ O ₂) ₃	Powder	
Vanadium	V(C ₅ H ₇ O ₂) ₃	Powder	
Ytterbium	Yb(C ₅ H ₇ O ₂) ₃	Powder	
Yttrium	Y(C ₅ H ₇ O ₂) ₃	Powder	
Zinc	Zn(C ₅ H ₇ O ₂) ₂	Needle	138 (s)
Zirconium	Zr(C ₅ H ₇ O ₂) ₄	White crystal	172

Note: (s) indicates that the compound sublimes at atmospheric pressure before melting.

5.1 Aluminum^{[10][11]}

Decomposition of the following alkyls at 200–300°C up to 1 atm.

- Trimethyl aluminum, $(\text{CH}_3)_3\text{Al}$ or TMA.
- Triethyl aluminum, $(\text{C}_2\text{H}_5)_3\text{Al}$ or TEA.
- Tri-isobutyl aluminum, $(\text{C}_4\text{H}_9)_3\text{Al}$ or TIBA.
- Dimethyl aluminum hydride, $(\text{CH}_3)_2\text{AlH}$ or DMAH (preferred reaction).

5.2 Cadmium^[13]

- Decomposition of dimethyl cadmium, $\text{Cd}(\text{CH}_3)_2$, at 10 Torr with argon laser.

5.3 Chromium^{[14][15]}

- Decomposition of dicumene chromium, $(\text{C}_9\text{H}_{12})_2\text{Cr}$, at 320–545°C (possible inclusion of carbon or hydrogen in the deposit).

5.4 Copper^{[16]–[18]}

- Decomposition of copper acetylacetonate, $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$ at 260–340°C.
- Hydrogen reduction of copper chelate, $\text{Cu}(\text{C}_5\text{HF}_6\text{O}_2)_2$ at 250°C.
- Decomposition of copper hexafluoroacetylacetonate at 200°C.

5.5 Gold^[19]

- Decomposition of dimethyl 1-2,4 pentadionate gold, or dimethyl-(1,1,1-trifluoro-2-4-pentadionate) gold, or dimethyl-(1,1,1-5,5,5 hexafluoro 2-4 pentadionate) gold.

5.6. Nickel^[20]

- Hydrogen reduction of nickel alkyl, $\text{Ni}(\text{C}_5\text{H}_5)_2$ at 200°C, or nickel chelate, $\text{Ni}(\text{C}_5\text{HF}_6\text{O}_2)_2$ at 250°C.

5.7. Platinum^{[13][21]}

- Decomposition of platinum hexafluoro-2,4-pentadionate, $\text{Pt}(\text{CF}_3\text{COCHCOCF}_3)_2$, or tetrakis-trifluorophosphine, $\text{Pt}(\text{PF}_3)_4$ at 200–300°C in hydrogen.

5.8. Iridium^{[22][23]}

- Decomposition of acetyl acetate, $\text{Ir}(\text{CH}_3\text{COCHCOCH}_3)_3$ at 400–450°C and 1 atm.

5.9. Rhodium^[22]

- Decomposition of rhodium acetyl acetate, $\text{Rh}(\text{CH}_3\text{COCHCOCH}_3)_3$ at 250°C and 1 atm. Decomposition of rhodium trifluoro-acetyl acetate, $\text{Rh}(\text{C}_5\text{H}_4\text{F}_3\text{O}_2)_3$ at 400°C and 1 atm.

5.10 Tin^[24]

- Decomposition of tetramethyl or triethyl tin, $\text{Sn}(\text{CH}_3)_4$, $\text{Sn}_2(\text{C}_2\text{H}_5)_3$ at 500–600°C at low pressure.

5.11 Titanium^{[25][26]}

- Decomposition of tris-(2.2'-bipyridine) titanium at < 600°C (deposit tends to retain impurities such as C, N_2 , and H_2).

6.0 MOCVD REACTIONS FOR THE DEPOSITION OF CARBIDES AND NITRIDES

Many CVD reactions are being investigated for the deposition of carbides and nitrides, particularly for titanium nitride for semiconductor applications, such as diffusion barrier. The following is a summary of the metallo-organic precursors and deposition condition presently used in development or production of these materials.

6.1 Chromium Carbide^[27]

- Decomposition of chromium dicumene $\text{Cr}[(\text{C}_6\text{H}_5)\text{C}_3\text{H}_7]_2$ at 300–550°C and 0.5–50 Torr.

6.2 Titanium Carbide^[28]

- Decomposition of tris-(2.2'-bipyridine) titanium at 370–520°C.
- Decomposition of tetraneopentyl titanium at 150–300°C.

- Decomposition of dichlorotitacene, $(C_5H_5)_2TiCl_2$, (substrate temperature is 700°C).

6.3 Aluminum Nitride^{[29]–[32]}

- Reaction of ammonia (NH_3) with trimethyl aluminum $(CH_3)_3Al$ at 900°C and < 1 Torr).
- Pyrolysis of diethyl aluminum azide $[(C_2H_5)_2AlN_3]$ at 450–870°C).
- Pyrolysis of hexakis(dimethylamido)dialuminum with ammonia at 200–250°C at 1 atm.

6.4 Boron Nitride^[33]

- Reaction of ammonia (NH_3) with triethyl boron $B(C_2H_5)_3$ in a H_2 and Ar at 750–1200°C.

6.5 Silicon Nitride^[34]

- Reaction of ammonia (NH_3) with tetrakis(dimethylamido)silicon, $Si(NMe_2)_4$ at 200–400°C.

6.6 Titanium Nitride^{[35]–[38]}

- Reaction of tetrakis-diethylamino titanium (TDEAT) or tetrakis-dimethylamino titanium (TDMAT) with ammonia (NH_3) at 300°C in a flow of helium. Possible carbon retention.
- Pyrolysis of tetrakis(dimethylamido)titanium (TDMAT) in nitrogen at 300°C.

7.0 MOCVD REACTIONS FOR THE DEPOSITION OF OXIDES

7.1 Aluminum Oxide^[39]

- Pyrolysis of aluminum isopropoxide, $\text{Al}(\text{OC}_3\text{H}_7)_3$ at 900°C .
- Decomposition of aluminum alkyls, such as $(\text{CH}_3)_3\text{Al}$ or $(\text{C}_2\text{H}_5)_3\text{Al}$ in O_2 or N_2O at $250\text{--}500^\circ\text{C}$.

7.2 Chromium Oxide^[40]

- Decomposition of chromium acetyl acetonate, $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ at $520\text{--}560^\circ\text{C}$.

7.3 Hafnium Oxide^[41]

- Pyrolysis of hafnium acetylacetonate, $\text{Hf}(\text{C}_5\text{H}_7\text{O}_2)_3$, at $400\text{--}750^\circ\text{C}$ or hafnium trifluoro-acetylacetonate, $\text{Hf}(\text{C}_5\text{H}_4\text{O}_2\text{F}_3)_4$ at $500\text{--}550^\circ\text{C}$ with helium and oxygen as carrier gases.

7.4 Iron Oxide^[42]

- Decomposition of acetylacetonate, $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$, at $400\text{--}500^\circ\text{C}$, or of the iron trifluoro-acetylacetonate, $\text{Fe}(\text{F}_3\text{C}_5\text{H}_4)_3$, at 300°C in oxygen.
- Decomposition of iron cyclopentadienyl, $(\text{C}_5\text{H}_5)_2\text{Fe}$, in O_2 at $300\text{--}500^\circ\text{C}$ and 1–20 Torr.

7.5 Silicon Dioxide^{[43]–[47]}

- Decomposition of tetraethyl orthosilicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$, at 700°C and <1 Torr, in the presence of ozone.
- Decomposition of diacetoxy-ditertiarybutoxy silane (DADBS) at 450–550°C and <1 Torr.
- Decomposition of octamethyl-cyclotetrasiloxane in ozone at 400°C at low pressure.

7.6 Tantalum Oxide^{[48][49]}

- Pyrolysis of tantalum ethylate, $\text{Ta}(\text{OC}_2\text{H}_5)_5$, in O_2 and nitrogen at 340–450°C and <1 Torr.
- Pyrolysis of tantalum dichlorodiethoxyacetylacetonate at 300–500°C.

7.7 Tin Oxide^{[50]–[52]}

- Oxidation of tetramethyl tin at atmospheric pressure or <1 Torr) at 350–600°C.
- Reaction of dimethyl tin chloride, $(\text{CH}_3)_2\text{SnCl}_2$, with O_2 at 540°C.

7.8 Titanium Oxide^{[53][54]}

- Pyrolysis of titanium ethoxide, $\text{Ti}(\text{OC}_2\text{H}_5)_4$ in O_2 and He at 450°C.
- Pyrolysis on titanium tetraisopropoxide, $\text{Ti}(\text{OC}_3\text{H}_7)_4$ in O_2 at 300°C and <1 Torr.

7.9 Zinc Oxide^[55]

- Reaction of dimethyl zinc and tetrahydrofuran (THF) at 300–500°C, at low pressure.

7.10 Zirconium Oxide^{[56][57]}

- Yttria-stabilized zirconia by codeposition of tetramethyl heptadione of zirconium and yttrium, $\text{Zr}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$ and $\text{Y}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$ at 735°C.
- Decomposition of the trifluoro-acetylacetonates in He above 300°C.

7.11 Titanates^{[58]–[61]}

- Lead titanate (PbTiO_3) by reacting ethyl titanate and lead vapor in oxygen and nitrogen at 500–800°C.
- Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) by reacting triphenyl bismuth, $\text{Bi}(\text{C}_6\text{H}_5)_3$ and titanium isopropoxide at 600–800°C and 5 Torr.
- Strontium titanate (SrTiO_3) by reacting titanium isopropoxide and a strontium beta-diketonate complex at 600–850°C and 5 Torr.

7.12 Superconductors^{[62][83]}

- $\text{YBa}_2\text{Cu}_3\text{O}_7$ from acetylacetonates (tetramethyl heptadionate) of yttrium, barium, and copper, at 825°C and 5 Torr.

8.0 MOCVD REACTIONS FOR THE DEPOSITION OF III–V AND II–VI COMPOUNDS

Note: See Ch. 12 for more details

8.1 III–V Compounds^{[64][65]}

- Reaction of an alkyl (usually trimethyl) of Group-IIIb element (Al, Ga, In) with a hydride of a Group-Vb element (P, As, Sb) at 600–800°C and 1 atm.^{[41][42]} P-doping obtained from addition of diethyl zinc or bis(cyclopentadienyl) magnesium.

8.2 II–VI Compounds

- Reaction of a vaporized metal of Group II (Zn, Cd, Hg) and alkyl of Group VI element (Te, Se) at 325–350°C.

9.0 GENERAL APPLICATIONS OF MOCVD

Table 4.3. is a summary of the major applications of MOCVD. More details are found in Chs. 13–16.^[2]

Table 4.3.
Applications of MOCVD

GaAs/AlGaAs photocathodes, solar cells, lasers, HEMATs,
high-power LEDs, MESFETs
InP/InGaAsP long-wavelength lasers and detectors
InP/InGaAs quantum wells, solar cells, detectors
GaAs on Si wafers
GaAs/InGaP HBTs
GaAs/AlGaInP visible lasers, orange LEDs
HgCdTe detectors

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5

CVD Processes and Equipment

1.0 INTRODUCTION

1.1 CVD Processes

The factors controlling a CVD process are:

- Thermodynamic, mass transport, and kinetic considerations, which are reviewed in Ch. 2.
- The chemistry of the reaction, which is reviewed in Chs. 3 and 4.
- The processing parameters of temperature, pressure, and chemical activity, which are reviewed in this chapter.

The various CVD processes comprise what is generally known as thermal CVD, which is the original process, laser and photo CVD, and more importantly plasma CVD, which has many advantages and has seen a rapid development in the last few years. The difference between these processes is the method of applying the energy required for the CVD reaction to take place.

1.2 CVD Coatings

Coatings are by far the largest area of application of CVD at the present but by no means the only CVD process. Other areas of CVD, such as production of powders, fibers, monoliths, and composites, are growing rapidly.

CVD/PVD thin films are usually considered as coatings having a thickness of less than ten microns. This is an arbitrary limitation and perhaps a better definition would be a coating that adds little if any mass to the substrate. Most thin films, in fact, are much less than $10\mu\text{m}$ and may be even less than $0.2\mu\text{m}$ in the newer semiconductor and optical designs, while some wear and erosion applications can be much thicker than $10\mu\text{m}$.

Coatings are used on a large scale in many production applications in optics, electronics, optoelectronics, tools, wear, and erosion and others. In the case of electronics and optoelectronics, practically all CVD applications are in the form of coatings.

1.3 Composite Nature of Coatings

The surface of a material exposed to the environment experiences wear, corrosion, radiation, electrical, or magnetic fields and other phenomena. It must have the properties needed to withstand the environment or to provide certain desirable properties, such as reflectivity, semiconductivity, high thermal conductivity, or erosion resistance. Depositing a coating on a substrate produces a composite material and, as such, allows it to have surface property, which can be entirely different from those of the bulk material.^[1]

2.0 CLOSED AND OPEN REACTOR

2.1 Closed Reactor

A CVD reaction can occur in one of two basic systems: the closed reactor or the open reactor (also known as close or open tube). The closed-reactor system, also known as chemical transport, was the first type to be used for the purification of metals. It is a hybrid process which combines vapor-phase transfer with solid-state diffusion. As the name implies, the chemicals are loaded in a container which is then tightly closed. A temperature differential is then applied which provides the driving force for the reaction.

Pack Cementation. A well-known close-reactor process is pack cementation, where the driving mechanism for the reaction is a difference in chemical activity at a given temperature. It is a effective process which is used industrially for boriding, chromizing, aluminizing, and siliconizing. It is shown schematically in Fig. 5.1.^{[2][3]} Although the process unquestionably involves vapor transfer reactions locally, these reactions are not controllable once the pack constituents and operating temperature have been chosen.

2.2 Open Reactor

As opposed to closed-reactor CVD, is the other CVD system is known as open-reactor or flowing-gas CVD, where the reactants are introduced continuously and flow through the reactor. Closed-reactor CVD is by far the most common system and will be referred to simply as CVD. It comprises three interrelated components:

- The reactant supply.
- The deposition system or reactor (the term reactor is universally used in CVD parlance to describe the vessel in which the reaction takes place and has nothing to do with a nuclear reactor).
- The exhaust system.

A typical CVD system is shown schematically in Fig. 5.2.

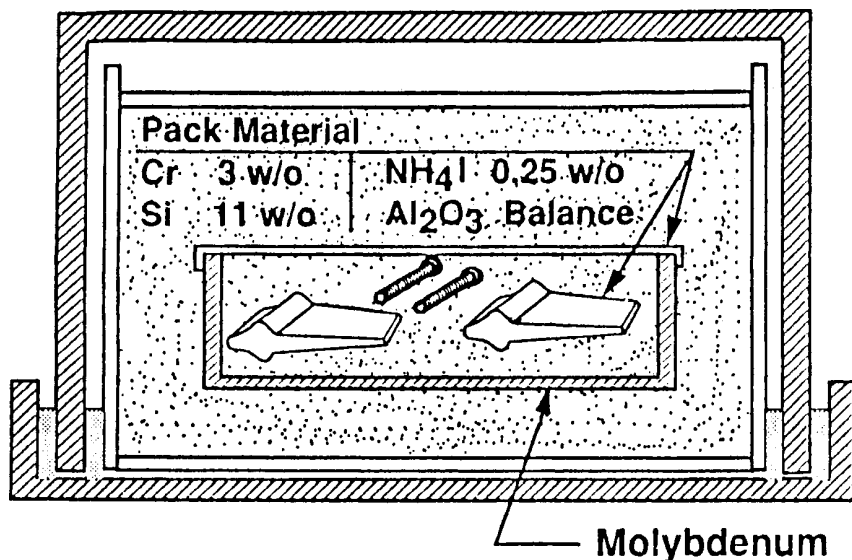


Figure 5.1. Schematic of pack-cementation chromizing apparatus.

3.0 REACTANT SUPPLY

3.1 Reactant Transport

Gases. The reactants (including diluent, extender, and carrier gases) must be transported and metered in a controlled manner into the reactor. In the case of gaseous reactants, this does not present any particular problem and is accomplished by means of pressure controllers, gauges, flowmeters, and mass-flow controllers.^{[4][5]}

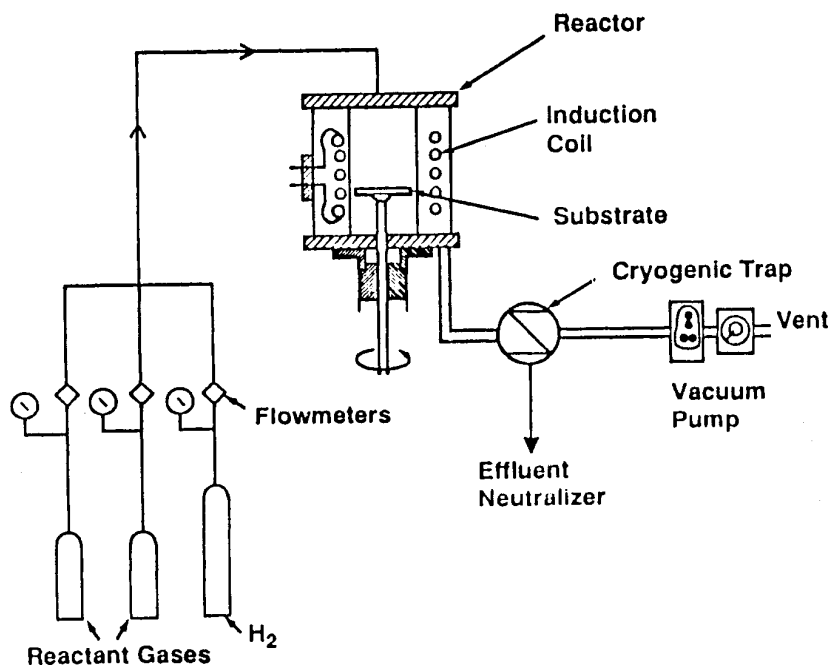


Figure 5.2. Schematic diagram of typical CVD apparatus.

Liquids. Many of the CVD reactants are liquid at room temperature.^[6] They must be heated to their evaporation temperature and transported into the reaction chamber by a carrier gas, which may be an inert gas such as argon, or another reactant such as hydrogen. If the vapor pressure of the liquid reactant is known, its partial pressure can be calculated and controlled by controlling the rate of flow and the volume of the carrier gas.

Flash vaporization is another simple delivery design, where the liquid is metered into a vessel heated above its boiling point (at the prevailing pressure). Controlled metering of the liquid into the vaporizer can be accomplished by a peristaltic pump or similar devices. A typical vaporizer to supply TiCl_4 is shown in Fig. 5.3.

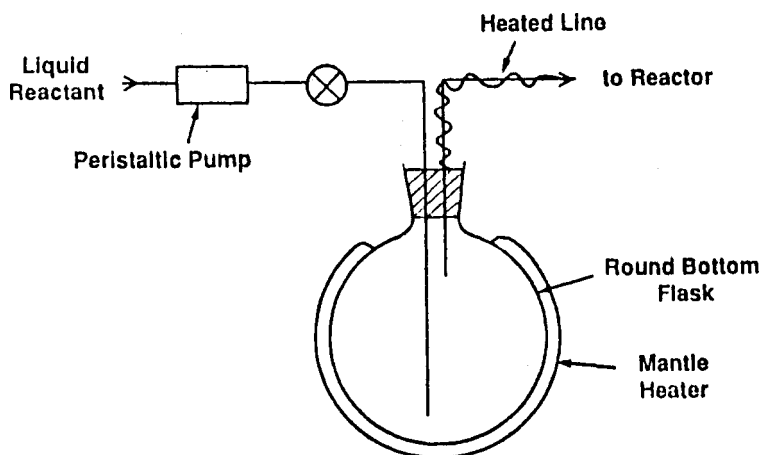


Figure 5.3. Vaporizer for liquid reactant.

Another delivery system is shown in Fig. 5.4, where a mass-flow controller injects a carrier gas into a heated bubbler. The carrier gas becomes saturated with the reactant vapor, which is then carried into the deposition chamber through a pressure controller and flowmeter.^[7]

Solids. Reactants which are solid at room temperature present more of a problem since they must be heated to their vaporization temperature, which in some cases may be relatively high. This is particularly true with metal halides as shown in Ch. 3, Table 3.3. It is often preferable to generate the reactant in situ. An example is the deposi-

tion of tungsten by the reduction of WCl_6 . The metal, in the form of chips, pellets, or powder, is placed in a chlorinator shown in Fig. 5.5, where the following reaction occurs:

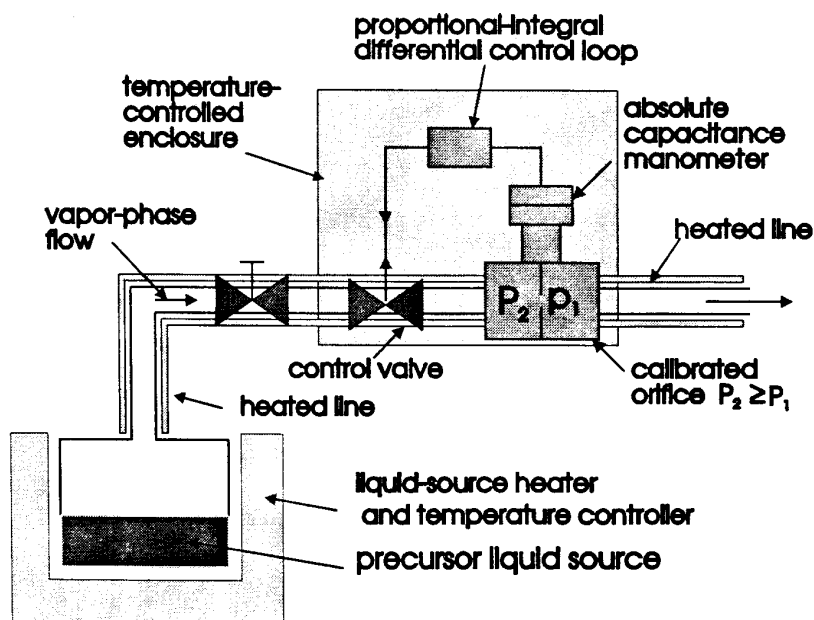


Figure 5.4. Bubbler with mass-flow controller.

The design of the chlorinator must be such that hydrogen cannot get into the chlorine supply and vice versa, otherwise an explosion may occur. For that reason, chlorine is usually metered with an inert gas such as argon, and the hydrogen is introduced below the chlorinator. More hydrogen is required in the lower range of temperature and gradually less as the temperature is increased. Above 1000°C , WCl_6 decomposes without the need for any hydrogen.

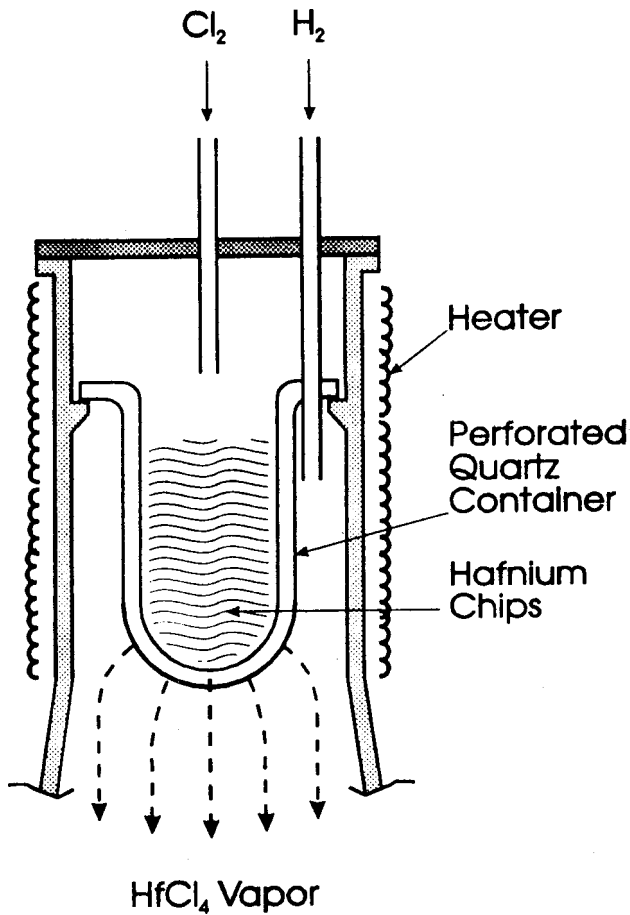


Figure 5.5. In situ chlorinator for the generation of hafnium chloride.

The amount of tungsten chloride generated in Reaction (1) is a function of the surface area of the tungsten chips and will be gradually reduced as the reaction proceeds and will eventually stop when all the metal has been chlorinated.

3.2 Reactant Purity and Contamination

The requirements placed on the performance and reliability of CVD coatings are continuously upgraded. For one thing, this means the need for an ever increasing degree of purity of the precursor materials since impurities are the major source of defects in the deposit. The purity of a gas is expressed in terms of nines, for instance, six nines, meaning a gas that is 99.9999% pure, which is now a common requirement. It is also expressed in ppm (parts per million) or ppb (parts per billion) of impurity content.

Suppliers of precursor materials are well aware of this problem and are making considerable efforts to improve their products, usually at a greatly increased cost. However, using a pure reactant is not sufficient since a gas can become contaminated again as it leaves its storage container and travels through the distribution system to the reactor chamber. It can pick up moisture, oxygen, particles, and other contaminants even if gas-tight metal lines are used. For that reason, it is often recommended to purify and filter the gases at the point of use, i.e., just before entering the reaction zone.^{[8]–[10]}

There are several methods used to purify gases: catalytic adsorption, palladium diffusion, gettering, chemisorption, and filtration.^[11]

Catalytic Adsorption. This method can reduce impurities, such as H₂, O₂, CO, and hydrocarbons, to less than 10 ppb. The catalyst converts these impurities into CO₂, H₂O, and other species that can then be removed by molecular sieves and cryogenic adsorption.

Palladium Diffusion. Palladium is very permeable to hydrogen but not permeable to other gases. As a result, it is a useful hydrogen purifier. A palladium membrane, heated to 400 °C, purifies hydrogen to <10 ppb but requires a high pressure differential for net diffusion to take place at reasonable rates of hydrogen supply.

Gettering. Gettering materials, such as zirconium or titanium alloys, are heated to 400°C. At that temperature, they react with the impurities in the gas stream such as O₂, H₂O, N₂, H₂, CO, CO₂, and hydrocarbons. Total impurities can be reduced to <100 ppb.

Chemisorption. This process uses resins, which are chemically treated with metallo-organics and which are discarded after depletion.

Filtering. This is the final step after purification. Polymers, such as Teflon, are used widely in filters but, because of problems with their outgassing, are being increasingly replaced by ceramic and metal filters.

4.0 THERMAL CVD: DEPOSITION SYSTEM AND REACTOR DESIGN

As stated in the introduction to this chapter, CVD can be classified by the method used to apply the energy necessary to activate the CVD reaction, i.e., temperature, photon, or plasma. This section is a review of temperature-activation process commonly known as thermal CVD.

4.1 Heating Methods

Thermal CVD requires high temperature, generally from 800 to 2000°C, which can be generated by resistance heating, high-frequency induction, radiant heating, hot plate heating, or any combination of these. Thermal CVD can be divided into two basic systems known as hot-wall reactor and cold-wall reactor (these can be either horizontal or vertical).

Hot-Wall Reactors. A hot-wall reactor is essentially an isothermal furnace, which is often heated by resistance elements. The parts to be coated are loaded in the reactor, the temperature is raised to the desired level, and the reaction gases are introduced. Figure 5.6 shows such a furnace which is used for the coating of cutting tools with TiC, TiN, and Ti(CN). These materials can be deposited alternatively under precisely controlled conditions. Such reactors are often large and the coating of hundreds of parts in one operation is possible (see Ch. 18).

In some cases, the parts to be coated (such as semiconductor silicon wafers) are stacked vertically. This minimizes particle contamination and considerably increases the loading capacity (as opposed to horizontal loading).

Hot wall reactors have the advantage of close temperature control. A disadvantage is that deposition occurs everywhere, on the part as well as on the walls of the reactor, which require periodic cleaning or the use of a disposable liner.

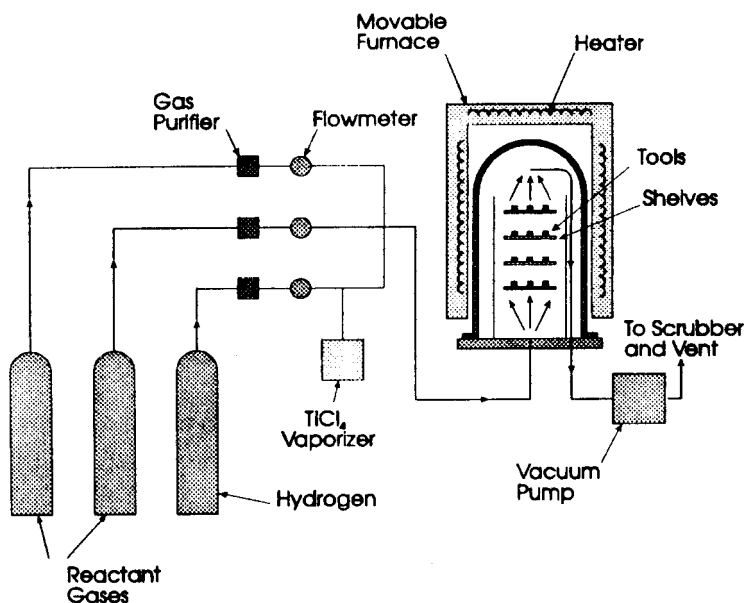


Figure 5.6. Production CVD reactor for the coating of cutting tools.

Cold-Wall Reactors. In a cold-wall reactor, the substrate to be coated is heated directly either by induction or by radiant heating while the rest of the reactor remains cool, or at least cooler. Most CVD reactions are endothermic, i.e., they absorb heat and deposition takes place preferentially on the surfaces where the temperature is the highest, in this case the substrate. The walls of the reactor, which are cooler, remain uncoated. A simple laboratory-type reactor is shown

in Fig. 5.7. It is used for the deposition of tungsten on a graphite substrate using in situ chlorination. It is heated by high-frequency induction (45 MHz) and operates at low pressure (5 Torr). The part is rotated to improve deposition uniformity.

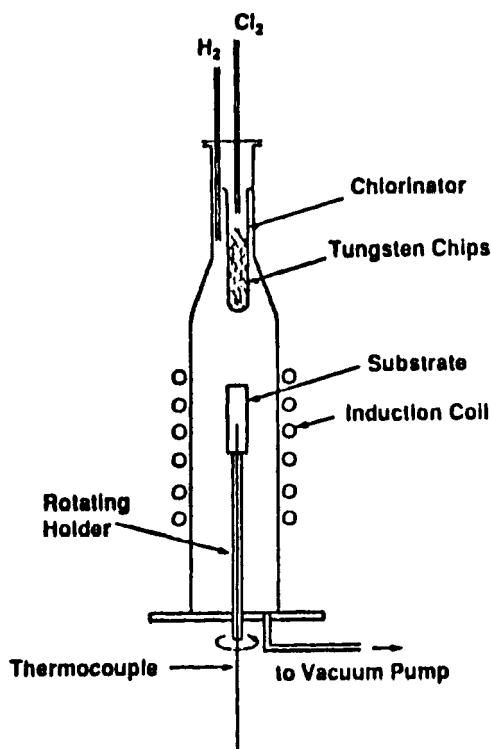


Figure 5.7. Cold-wall laboratory reactor for tungsten deposition.

A more elaborate example of induction heating is shown in Fig. 5.8, which shows a reactor designed for the deposition of silicon epitaxy in semiconductor devices (see Ch. 13). The power is supplied by a solid-state high-frequency (20 KHz) generator. A radiation reflector, shown in Detail A, increases the efficiency and uniformity of deposition. Pressure varies from 100 mbar to 1 atm.

Another example of a cold-wall reactor is shown in Fig. 5.9. It uses a hot plate and a conveyor belt for continuous operation at atmospheric pressure. Preheating and cooling zones reduce the possibility of thermal shock. The system is used extensively for high-volume production of silicon-dioxide coatings for semiconductor passivation and interlayer dielectrics.

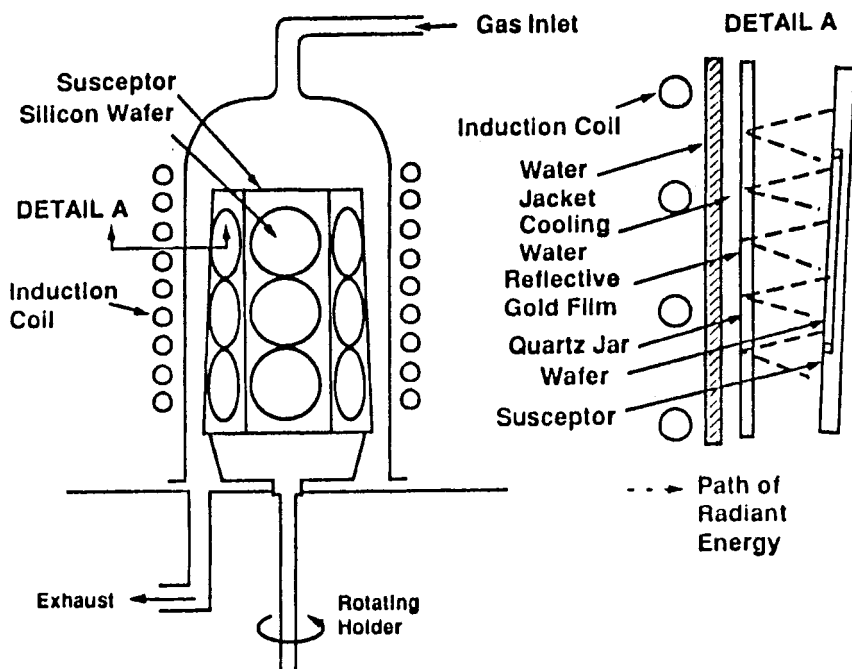


Figure 5.8. Schematic of cold-wall production reactor for silicon epitaxy.

Radiant heating, which in the past has been used mostly in experimental reactors, is gradually being introduced into production systems. The basic design is shown in Fig. 5.10. It is, of course, essential that the walls of the reactor be transparent to radiation and remain so during the deposition sequence, so that heating can proceed unhindered.

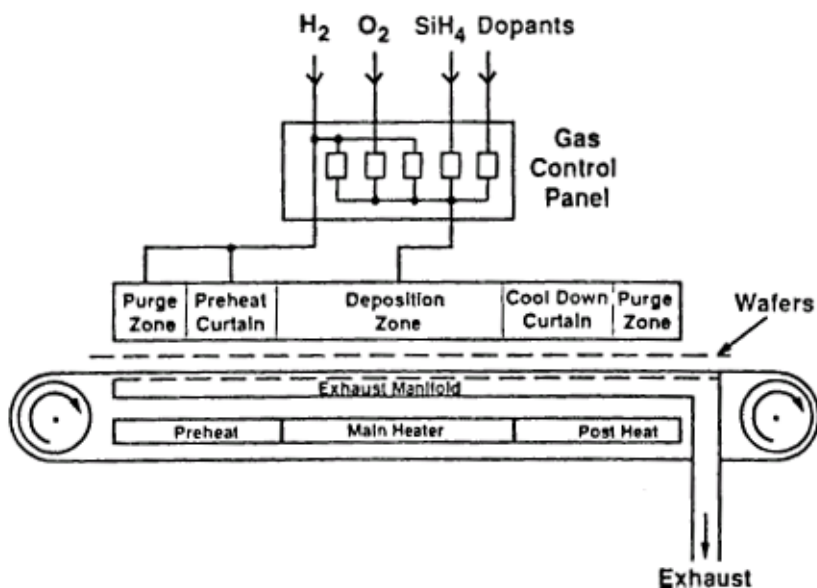


Figure 5.9. Continuous operation cold-wall reactor for atmospheric pressure deposition of SiO_2 .

4.2 Atmospheric and Low-Pressure Reactors

As shown in Ch. 2, the effect of pressure on the nature of the deposit is considerable. At high pressure (i.e., ca. atmospheric), the deposition is diffusion limited and, at low pressure, surface reaction is the determining factor. In practical terms, this means that low pressure generally provides deposits with greater uniformity, better step coverage, and improved quality.

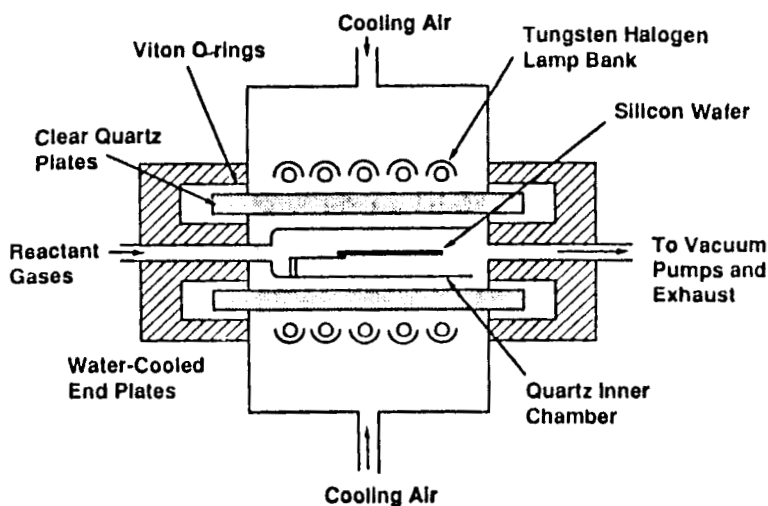


Figure 5.10. Cold-wall reactor with radiant heating.

Some reactants in atmospheric-pressure reactors must be highly diluted with inert gases to prevent vapor-phase precipitation, while generally no dilution is necessary at low pressure. However, atmospheric pressure reactors are simpler and cheaper. They can operate faster, on a continuous basis and, with recent design improvements, the quality of the deposits has been upgraded considerably and satisfactory deposits of many materials, such as oxides, are obtained.

Ultra-High Vacuum Reactors. CVD reactions at extremely low pressures (i.e., 10^{-5} Torr) are being developed for the deposition of semiconductor materials, such as silicon-germanium and some optoelectronic materials. Advantages appear to be better control of the deposit structure and reduction of impurities.^{[12][13]}

Typical Reactor Design. Table 5.1 lists typical CVD production reactors which include cold-wall and hot-wall reactors operating at low or atmospheric pressures. The decision to use a given system should be made after giving due consideration to all the factors of cost, efficiency, production rate, ease of operation, and quality.

A typical production reactor for the atmospheric deposition of SiO_2 and boro-phospho-silicate glass is shown in Fig. 5.11.

Table 5.1 Reactor Designs and Typical Production Applications			
Coating Type	Application	Reactor Type	Pressure
BPSG (boro-phospho-silicate glass)	passivation of semiconductors	cold wall	ca. 1 Torr
Silicon epitaxy	semiconductors	cold wall	80 Torr to 1 atm
SiO_2	passivation of semiconductors	cold wall	1 atm
TiC, TiN, Ti(CN)	cutting tools	hot wall	1 Torr
Doped silicon	semiconductors	hot wall	1 Torr
TiO_2	solar cells	cold wall	1 atm
Tungsten silicide	gates & inter-connections of semiconductors	cold wall	1 Torr

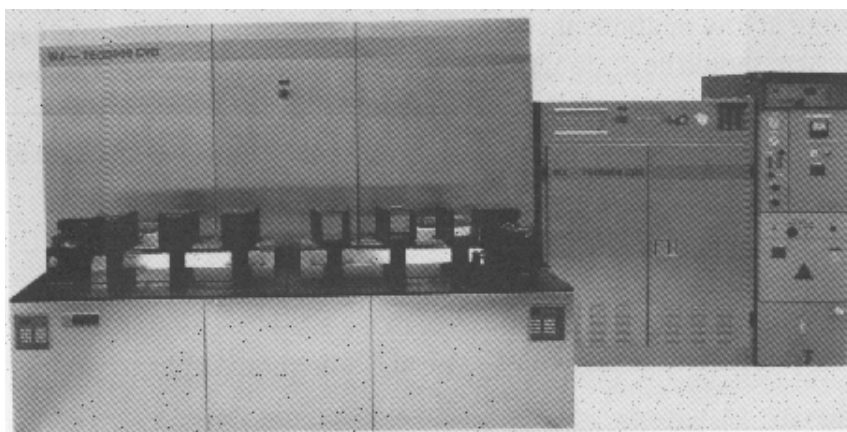


Figure 5.11. Atmospheric deposition equipment for SiO_2 and glass. (Source: Watkins-Johnson, Palo Alto, CA)

5.0 EXHAUST AND BY-PRODUCT DISPOSAL

CVD does not usually require the low pressures which are necessary with sputtering, MBE, and other PVD processes. Consequently the vacuum system is simpler and less costly. Mechanical pumps are adequate for many operations. Vane pumps, built with corrosion resistant material, are preferred. If properly maintained, these pumps will operate for long periods of time.

A major disadvantage of CVD (as opposed to PVD) is that many precursors are toxic and in some cases lethal even at low concentration (for instance nickel carbonyl, diborane, arsine, and phosphine). Some are also pyrophoric, such as silane, some alkyls, arsine, and phosphine. Very often the reaction is not complete and some of the precursor materials may reach the exhaust unreacted. In addition, many of the by-products of the reaction are also toxic and corrosive. This means that all these effluents must be eliminated or neutralized before they are released to the

environment. Careful design and construction of the exhaust system are essential.

A typical exhaust manifold is shown in Fig. 5.12.^[14] It includes a particle trap, which collects solid particles originating in the reactor, which might otherwise damage the pump. The trap also prevents backstreaming of pump oil into the reactor and subsequent contamination. Also in the manifold are a gate valve and a pressure indicator and sensor. If high gas velocity is required in the reactor, a roots pump is included upstream from the vane pump. Downstream from the vane pump, the exhaust gases pass through an oil demister and a scrubber, where they are treated and neutralized. Also commonly used are incinerating systems for the decomposition of toxic gases, such as silane, phosphine, and diborane.

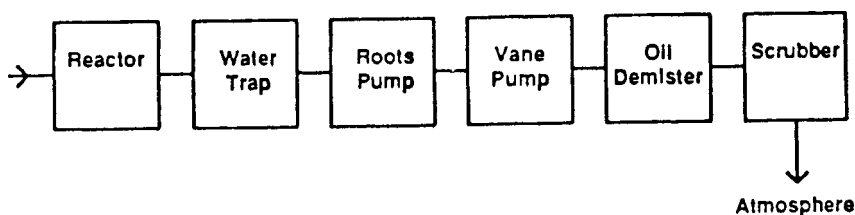


Figure 5.12. Schematic of exhaust system

Exhaust conditioning requires a precise identification of all the gases and liquids, both residual precursors and by-products. It also requires leak-tight piping and ducts, and suitable mechanical and chemical scrubbers to remove or neutralize dangerous materials and the proper venting of the mechanical pump with a stainless exhaust filter to remove oil mist at the source.^[15]

6.0 LASER AND PHOTO CVD

Two methods based on photon activation have recently been developed: laser and photo CVD. These methods are still essentially in the experimental stage.

6.1 Laser CVD

A laser produces a coherent, monochromatic high-energy beam of photons, which can be used effectively to activate a CVD reaction. Laser CVD occurs as a result of the thermal energy from the laser coming in contact with and heating an absorbing substrate. The wavelength of the laser is such that little or no energy is absorbed by the gas molecules. The substrate is locally heated in a manner analogous to the local heating in a cold-wall reactor and deposition is restricted to the heated area as shown in Fig. 5.13, which illustrates the deposition of a thin stripe.

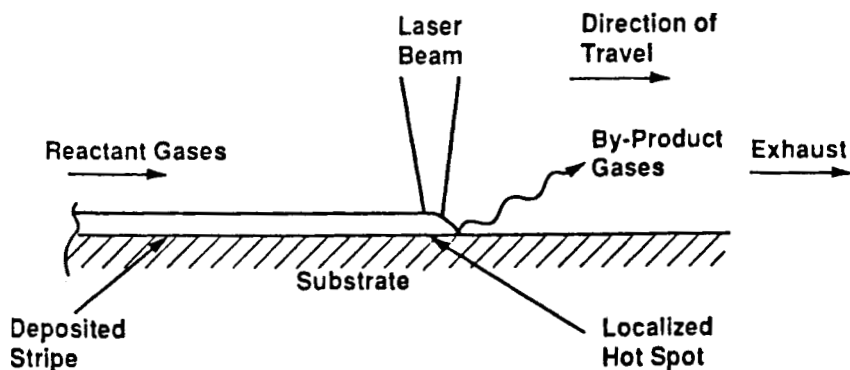


Figure 5.13. Schematic of laser-CVD growth mechanism (stripe deposition).

Laser CVD involves essentially the same deposition mechanism and chemistry as conventional thermal CVD and theoretically the same wide range of materials can be deposited. Some examples of materials deposited by laser CVD are listed in Table 5.2.^{[16]–[18]}

Table 5.2
Examples of Materials Deposited by Thermal Laser CVD^{[15][16][17]}

Materials	Reactants	Pressure	Laser (nm)
Aluminum	$\text{Al}_2(\text{CH}_3)_6$	10 Torr	Kr (476–647)
Carbon	$\text{C}_2\text{H}_2, \text{C}_2\text{H}_6, \text{CH}_4$		Ar-Kr (488–647)
Cadmium	$\text{Cd}(\text{CH}_3)_2$	10 Torr	Kr (476–647)
Gallium Arsenide	$\text{Ga}(\text{CH}_3)_3, \text{AsH}_3$		Nd: YAG
Gold	$\text{Au}(\text{ac.ac.})$	1 Torr	Ar
Indium oxide	$(\text{CH}_3)_3\text{In}, \text{O}_2$		ArF
Nickel	$\text{Ni}(\text{CO})_4$	350 Torr	Kr (476–647)
Platinum	$\text{Pt}(\text{CF}(\text{CF}_3\text{COCHCOCF}_3)_2)$		Ar
Silicon	$\text{SiH}_4, \text{Si}_2\text{H}_6$	1 atm	Ar-Kr (488–647)
Silicon oxide	$\text{SiH}_4, \text{N}_2\text{O}$	1 atm	Kr (531)
Tin	$\text{Sn}(\text{CH}_3)_4$		Ar
Tin oxide	$(\text{CH}_3)_2\text{SnCl}_2, \text{O}_2$	1 atm	CO_2
Tungsten	WF_6, H_2	1 atm	Kr (476–531)
$\text{YBa}_2\text{Cu}_3\text{O}_x$	halides		Excimer

Experimental applications include the direct deposition of patterns as small as 0.5 μm in semiconductor applications using holographic methods, and the production of rods and coreless boron and silicon carbide fibers (see Ch. 19).

6.2 Photo CVD

In photo CVD, the chemical reaction is activated by the action of photons, specifically ultraviolet (UV) radiation, which have sufficient energy to break the chemical bonds in the reactant molecules. In many cases, these molecules have a broad electronic absorption band and they are readily excited by UV radiation. Although UV lamps have been used, more energy can be obtained from UV lasers, such as the excimer lasers, which have photon energy ranging from 3.4 eV (XeF laser) to 6.4 eV (ArF laser). A typical photo-laser CVD system is shown schematically in Fig. 5.14.^[17]

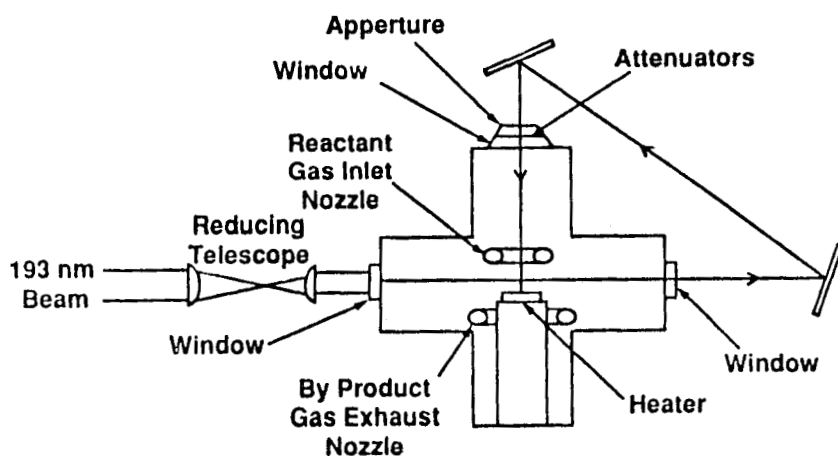


Figure 5.14. Schematic of photo-laser CVD apparatus.

No heat is required and the deposition may occur essentially at room temperature. Moreover, there is no constraint on the type of substrate, which can be opaque, absorbent, or transparent. A limitation of photo CVD is the slow rate of deposition, which has so far restricted its applications. Materials deposited on an experimental

basis include SiO_2 , Si_3N_4 , metal oxides, aluminum, tungsten, and other metals.

7.0 CHEMICAL VAPOR INFILTRATION (CVI)

CVI is a special CVD process in which the gaseous reactants penetrate (or infiltrate) a porous structure which acts as a substrate and which can be an inorganic open foam or a fibrous mat or weave. The deposition occurs on the fiber (or the foam) and the structure is gradually densified to form a composite.^{[19]–[22]} The chemistry and thermodynamics of CVI are essentially the same as CVD; but the kinetics is different, since the reactants have to diffuse inward through the porous structure and the by-products have to diffuse out.^[23] Thus, maximum penetration and degree of densification are attained in the kinetically limited low-temperature regime.

CVI is used to produce reinforced metal or ceramic composites and, in this respect, competes with standard ceramic and metallurgical processes, such as hot pressing and hot isostatic pressing. Such processes use high pressure and temperature and may cause mechanical and chemical damage to the substrate and its interface with the matrix. CVI, on the other hand, operates at low pressure and at temperatures lower than those required for the sintering of ceramics or the melting of metals, and the potential damage is considerably reduced.

A limitation of CVI is the necessity of interdiffusion of reactants and reaction products through relatively long, narrow, and sometimes tortuous channels. To avoid rapid deposition and choking of the entrance end of the channels, conditions are chosen to ensure deposition in the kinetically limited regime. This is a slow process which may take as much as several weeks before densification is achieved. In fact, full densification is almost impossible to obtain due to the formation of closed porosity.^[24]

Isothermal Infiltration. Several infiltration procedures have been developed, which are shown schematically in Fig. 5.15.^[23] In isothermal infiltration (5.15a), the gases surround the porous substrate and enter by diffusion. The concentration of reactants is higher toward the outside of the porous substrate, and deposition occurs preferentially in the outer portions forming a skin which impedes further infiltration. It is often necessary to interrupt the process and remove the skin by machining so that the interior of the substrate may be densified. In spite of this limitation, isothermal infiltration is used widely because it lends itself well to simultaneous processing of a great number of parts in large furnaces. It is used for the fabrication of carbon-carbon composites for aircraft brakes and silicon carbide composites for aerospace applications (see Ch. 19).

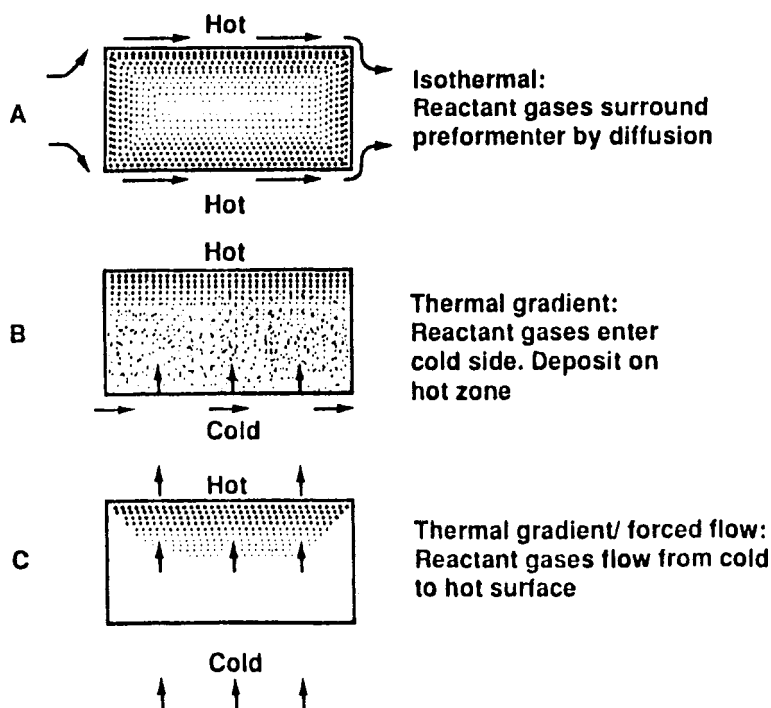


Figure 5.15. Chemical vapor infiltration (CVI) procedures.

Thermal-Gradient Infiltration. The principle of thermal-gradient infiltration is illustrated in Fig. 5.15b. The porous structure is heated on one side only. The gaseous reactants diffuse from the cold side and deposition occurs only in the hot zone. Infiltration then proceeds from the hot surface toward the cold surface. There is no need to machine any skin and densification can be almost complete. Although the process is slow since diffusion is the controlling factor, it has been used extensively for the fabrication of carbon-carbon composites, including large reentry nose cones.^[25]

Forced-Flow Infiltration. The principle of forced-flow, thermal-gradient infiltration is illustrated in Fig. 5.15c and Fig. 5.16.^[26] The gas inlet and the substrate are water cooled and only the top of the substrate is heated. The gaseous precursors enter under pressure (approximately 2 MPa back pressure) into the cool side of the substrate and flow through it to reach the hot zone where the deposition reaction takes place. The time to reach full densification is considerably reduced and final density is more uniform. This process is well suited for the fabrication of high strength silicon carbide ceramic composites but is limited to substrates of simple configuration and is difficult to adapt to the processing of multiple units.

8.0 FLUIDIZED-BED CVD

Fluidized-bed CVD is a special technique which is used primarily in coating particles, such as nuclear fuel. A flowing gas imparts quasi-fluid properties to the particles. Figure 5.17 shows a typical fluidized-bed CVD reactor.

The fluidizing gas is usually methane, helium, or another non-reactive gas. Factors to consider to obtain proper fluidization are the density and size of the particles to be coated, and the velocity, density, and viscosity of the gases.^[18] If the velocity is too low, the particles will fall into the gas inlet; if it is too high, they

will be blown out of the bed. Heavy or large objects may require suspension in the bed.

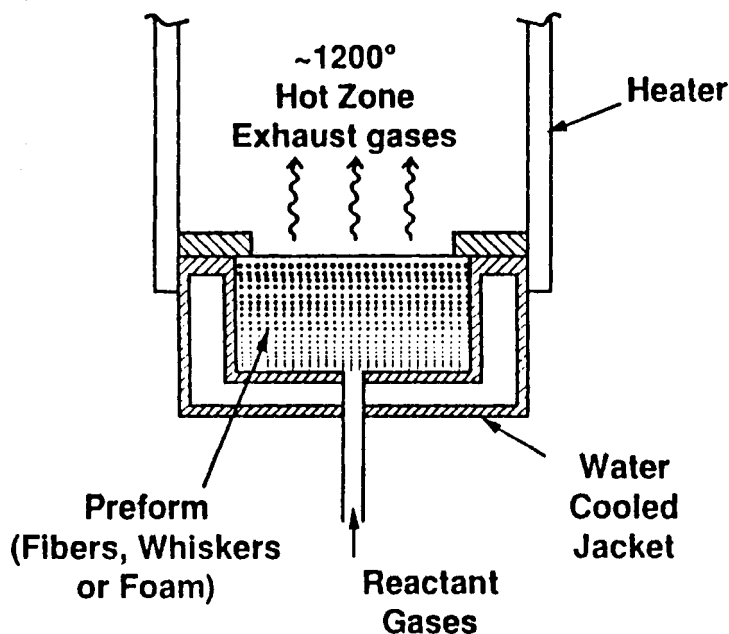


Figure 5.16. Forced-flow thermal-gradient chemical vapor infiltration.

As can be seen, two factors are particularly critical: (a) the density of the particle, since heavier particles are more difficult to fluidize, and (b) particle size, since the necessary gas velocity varies as the square of the particle diameter. The design of the reactor is also important since gas velocity at the top must be less than the terminal velocity of the particles, otherwise they would be blown out of the bed.^[28]

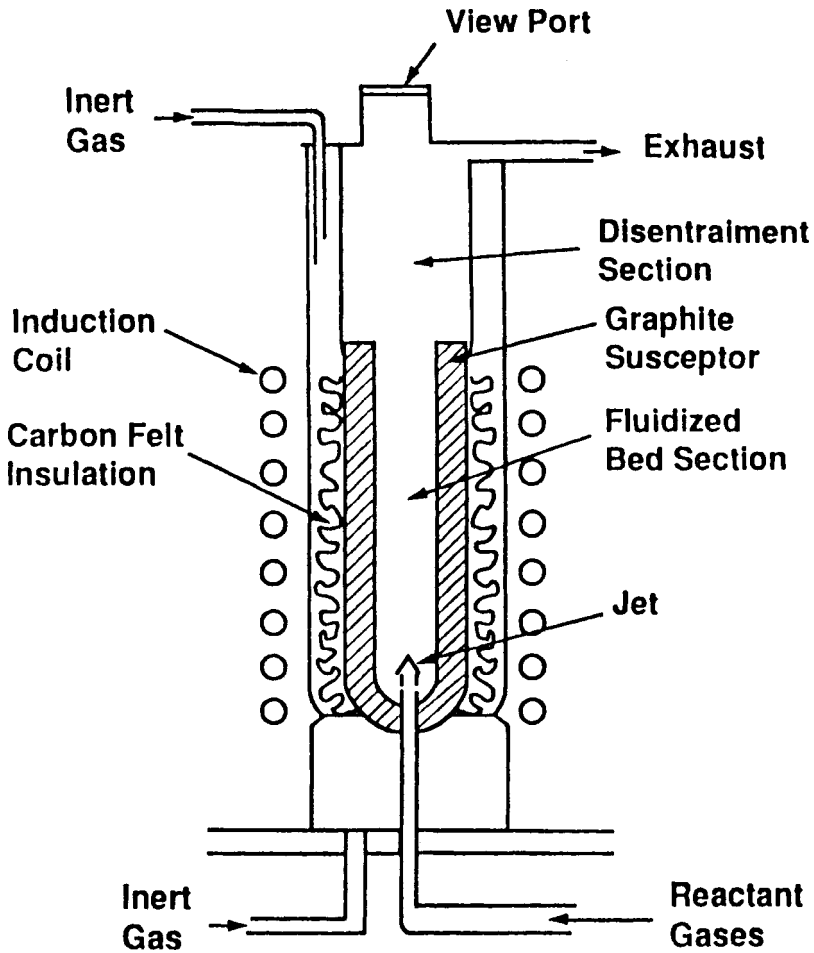


Figure 5.17. Fluidized-bed CVD reactor.

Fluidized-bed CVD was developed in the late 1950s for a specific application: the coating of nuclear-fuel particles for high temperature gas-cooled reactors.^[2] The particles are uranium-thorium carbide coated with pyrolytic carbon and silicon carbide for the purpose of containing the products of nuclear fission. The carbon is obtained from the decomposition of propane (C_3H_8) or propylene

(C_3H_6) at 1350°C , or methane (CH_4) at 1800°C . Methyltrichlorosilane (CH_3SiCl_3) is the preferred precursor for silicon carbide.

Other compounds have been deposited by fluidized-bed CVD including zirconium carbide (from ZrCl_4 and a hydrocarbon), hafnium carbide (from HfCl_4 and methane or propylene), and titanium carbide (from TiCl_3 and propylene).

9.0 PLASMA CVD

Thermal CVD, reviewed above, relies on thermal energy to activate the reaction, and deposition temperatures are usually high. In plasma CVD, also known as plasma-enhanced CVD (PECV) or plasma-assisted CVD (PACVD), the reaction is activated by a plasma and the deposition temperature is substantially lower. Plasma CVD combines a chemical and a physical process and may be said to bridge the gap between CVD and PVD. In this respect, it is similar to PVD processes operating in a chemical environment, such as reactive sputtering (see Appendix).

Plasma CVD was first developed in the 1960s for semiconductor applications, notably for the deposition of silicon nitride. The number and variety of applications have expanded greatly ever since and it is now a major process on par with thermal CVD.

9.1 Principles of Plasma Deposition

If a diatomic gas, for instance hydrogen, is heated above a given temperature, all the molecules (i.e., H_2) are dissociated into atoms ($\text{H}_2 \rightarrow 2\text{H}$) and eventually most if not all these atoms become ionized, that is they are stripped of their electrons and a plasma is formed which consists of ions (with positive charge), electrons (with negative charge), and atoms that have not been ionized (neutral).^[28] However, since ionization temperatures are usually extremely high ($>5000\text{K}$), a large amount of thermal energy is required. For example, although a

combustion flame may reach a maximum temperature of approximately 3700K, such a high temperature is not sufficient to completely ionize a gas such as hydrogen and in fact ionization only reaches about 10%.

A more convenient way to achieve a plasma is with electrical energy, such as a low-frequency discharge. By increasing the electrical energy in a fixed amount of gas, all molecules are eventually dissociated and complete ionization is achieved.

9.2 Types of Plasma

Two types of plasma are currently used in CVD: glow-discharge plasma (non-isothermal) and arc plasma (isothermal). Their characteristics are summarized in Table 5.3 and are described in more detail in the following sections.

Table 5.3
Characteristics of Plasmas^[28]

	Glow-Discharge	Arc
Plasma Type	Non-Isothermal (non-equilibrium)	Isothermal (equilibrium)
Frequency	3.45 MHz and 2.45 GHz (microwave)	≈ 1 MHz
Power	1–100 kW	1–20 MW
Flow rate	mg/sec	none
Electron concentration	10^9 – $10^{12}/\text{cm}^3$	$10^{14}/\text{cm}^3$
Pressure	200 Pa–0.15 atm	0.15–1 atm
Electron temperature	10^4K	10^4K
Atom temperature	500 K	10^4K

9.3 Glow-Discharge (Microwave) Plasma

A glow-discharge (non-isothermal) plasma is generated in a gas by a high-frequency electric field, such as microwave (2.45 GHz), at relatively low pressure.^[29] In such a plasma, the following events occur:

- In a high-frequency electric field, the gases are ionized into electrons and ions. The electrons, with their extremely small mass, are quickly accelerated to high-energy levels corresponding to 5000K or higher.
- The heavier ions with their much greater inertia cannot respond to the rapid changes in field direction. As a result, their temperature and that of the plasma remain low, as opposed to the electron temperature (hence the name non-isothermal plasma).
- The high-energy electrons collide with the gas molecules with resulting dissociation and generation of reactive chemical species and the initiation of the chemical reaction.

The most common frequencies in use for CVD are microwave (MW) at 2.45 GHz and, to a lesser degree, radio frequency (RF) at 13.45 MHz (the use of these frequencies must comply with federal regulations). A microwave-plasma deposition apparatus (for the deposition of polycrystalline diamond) is shown schematically in Fig. 5.18 (see Ch. 7, Sec. 3.4).

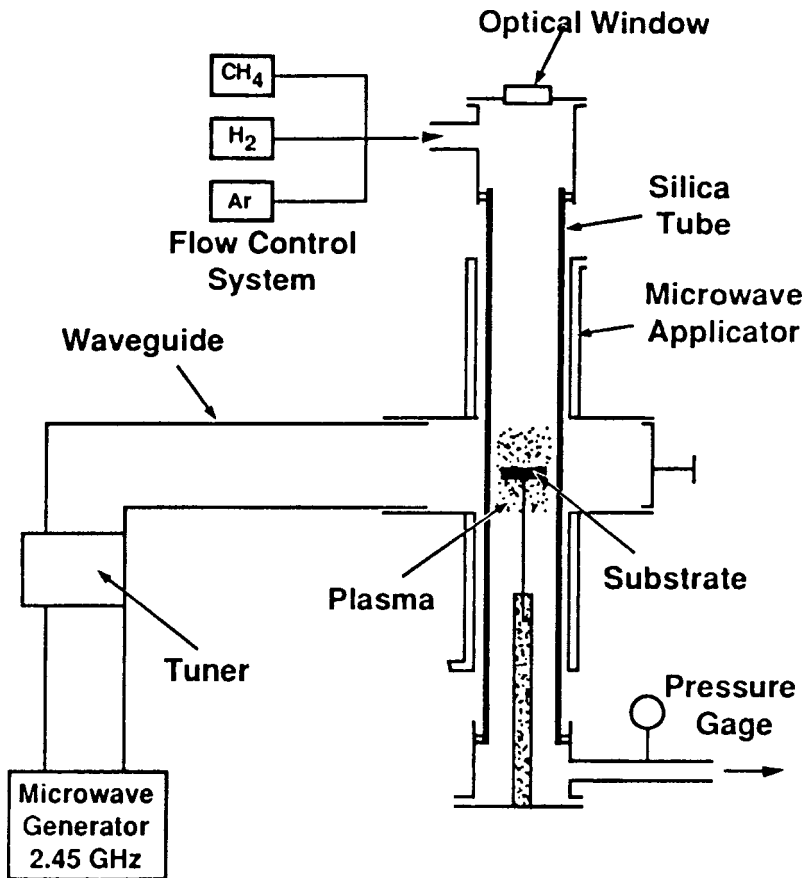


Figure 5.18. Microwave plasma apparatus for the deposition of diamond.

9.4 Electron Cyclotron Resonance (ECR)

A microwave plasma can also be produced by electron cyclotron resonance (ECR), through the proper combination of electric and magnetic fields.^{[30][31]} Cyclotron resonance is achieved when the frequency of the alternating electric field is made to match the natural frequency of the electrons orbiting the lines of force of the

magnetic field. This occurs at the standard microwave frequency of 2.45 GHz when it is coupled with a magnetic field of 875 Gauss. An ECR plasma reactor, suitable for the deposition of diamond, is shown schematically in Fig. 5.19 (see Ch. 7, Sec. 3.4).

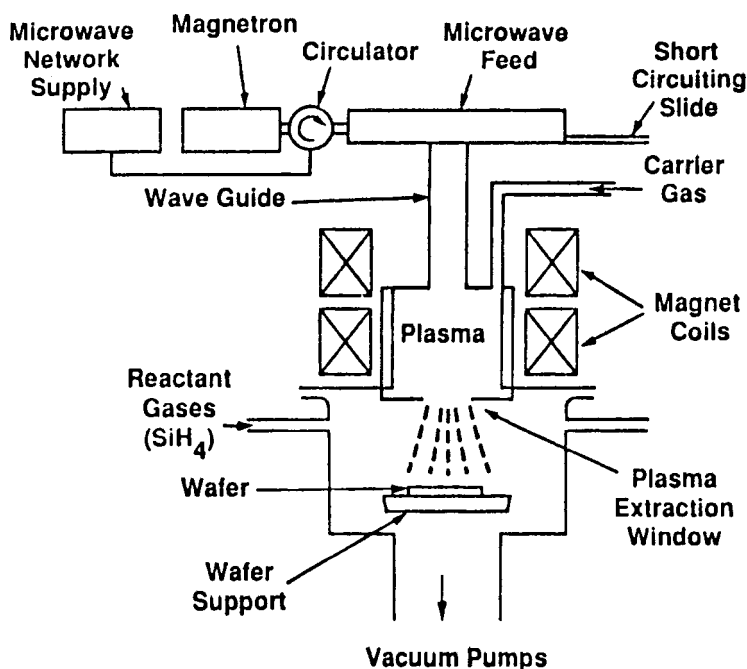


Figure 5.19. Schematic of electron cyclotron resonance (ECR) microwave deposition apparatus.

Advantages of ECR Plasma. An ECR plasma has two basic advantages:

- It minimizes the potential substrate damage caused by high-intensity ion bombardment, usually found in a standard high-frequency plasma where the ion energy may reach 100 eV.

- It minimizes the risk of damaging heat-sensitive substrates since it operates at a relatively low temperature (as low as 300°C in the case of SiO₂ deposition).

Limitations of ECR Plasma. The limitations of ECR plasma are a more difficult process control and more costly equipment due to the added complication of the magnetic field. In addition, lower pressure (10^{-3} to 10^{-5} Torr) is required, as opposed to 0.1 to 1 Torr for RF plasma deposition, as well as the need for a high-intensity magnetic field. Since there is the added variable of the magnetic field, the processing is more difficult to control.

9.5 RF Plasma

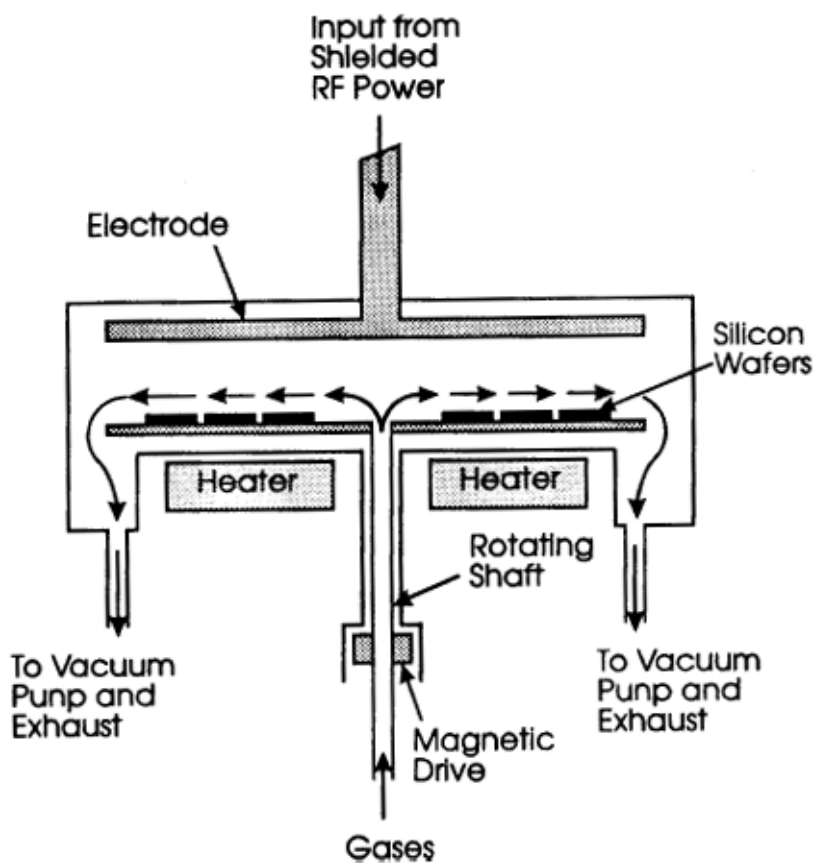
An RF plasma is generated at a frequency of 13.56 MHz. A typical equipment consists of parallel electrodes as shown in Fig. 5.20. It is a cold-wall design which is used extensively for the deposition of silicon nitride and silicon dioxide for semiconductor applications.

9.6 Arc Plasma

An arc plasma operates at lower frequency (ca. 1 MHz) than a glow-discharge plasma. Both electrons and ions respond to the constantly but relatively slowly changing field direction; they both acquire energy and their temperature is raised more or less equally. The plasma is in equilibrium (isothermal). Isothermal plasmas are generated at relatively high pressure (100 torr to 1 atm.). At such pressure, the mean free path, that is the average distance traveled by the gas species between collisions, is greatly reduced, collisions are more frequent, and molecules and ions heat readily.

An arc plasma requires a large amount of power and is extremely hot. For these reasons, it has not been used to any extent in

CVD deposition except for the special and important case of diamond deposition, a topic which is reviewed in Ch. 7.^{[32]–[34]}



9.7 Characteristics of Plasma CVD

Advantages of Plasma CVD. As shown in Table 5.4, with plasma CVD, a deposit is obtained at temperatures where no reaction whatsoever would take place in thermal CVD. This is its major advantage since it permits the coating of low-temperature sub-

strates, such as aluminum (which might otherwise melt), organic polymers (which would otherwise degrade and outgas) or of metals or metal alloys which experience structural changes at high temperature, such as austenitic steel. Dopants for semiconductors, such as boron and phosphorus, can also readily diffuse between buried layers of the device if the temperature exceeds 800°C, resulting in detrimental changes in the semiconductor properties. With plasma CVD these doped materials can be coated with little or no diffusion (see Ch. 13 and 14).

Table 5.4**Typical Deposition Temperatures for Thermal and Plasma CVD**

Material	Deposition Temperature (°C)	
	Thermal CVD	Plasma CVD
Epitaxial silicon	1000–1250	750
Polysilicon	650	200–400
Silicon nitride	900	300
Silicon dioxide	800–1100	300
Titanium carbide	900–1100	500
Titanium nitride	900–1100	500
Tungsten carbide	1000	325–525

Another advantage is that the effects of thermal expansion mismatch between substrate and coating and resulting stresses are reduced since the temperature of deposition remains low. In addition, the deposition rates are usually increased and, since the pressure is low (in the case of glow-discharge plasma CVD), the rate controlling factor is surface kinetics (see Ch. 2, which leads to greater uniformity. The low temperature of deposition also favors the formation of amorphous or very fine grained polycrystalline deposits which often have superior properties.

Limitations of Plasma CVD. With plasma CVD, it is difficult to obtain a deposit of pure material. In most cases, desorption of by-products and other gases is incomplete because of the low temperature and these gases, particularly hydrogen, remain as inclusions in the deposit. Moreover, in the case of compounds, such as nitrides, oxides, carbides, or silicides, stoichiometry is rarely achieved. This is generally detrimental since it alters the physical properties and reduces the resistance to chemical etching and radiation attack. However in some cases, it is advantageous; for instance, amorphous silicon used in solar cells has improved optoelectronic properties if hydrogen is present (see Ch. 15).

Plasma CVD tends to create undesirable compressive stresses in the deposit particularly at the lower frequencies.^[35] This may not be a problem in very thin films used in semiconductor applications, but in thicker films typical of metallurgical applications, the process is conducive to spalling and cracking.

Another disadvantage is that fragile substrates used in VLSI, such as some III–V and II–VI semiconductor materials, can be damaged by the ion bombardment from the plasma, particularly if the ion energy exceeds 20 eV. In addition, the plasma reacts strongly with the surface of the coating as it is deposited. This means that the deposition rate and often the film properties depend on the uniformity of the plasma. Areas of the substrate fully exposed will be more affected than the more sheltered ones. Finally, the equipment is generally more complicated and more expensive.

Overall the advantages of plasma CVD are considerable and it is used in an increasing number of applications as will be shown below.

9.8 Materials Deposited by Plasma CVD

The following table lists examples of plasma CVD materials and their applications.^{[29][35]}

Table 5.5
Examples of Plasma CVD Materials and Applications

Material Deposited	Common Precursors	Deposition Temp. °C	Applications	Status
a-Si	SiH ₄ -H ₂	250	semiconductor photovoltaic	production
Epitaxial silicon	SiH ₄	750	semiconductor	R & D
Si ₃ N ₄	SiH ₄ -N ₂ - NH ₃	300	passivation	production
SiO ₂	SiH ₄ -N ₂ O	300	passivation optical fiber decorative	production
Boro-phospho- silicate	SiH ₄ -TEOS- B ₂ H ₆ -PH ₃	355	passivation	semi- production
W	WF ₆	250–400	conductor in IC's	R & D
WSi ₂	WF ₆ -SiH ₄	230	conductor in IC's	semi- production
TiSi ₂	TiCl ₄ -SiH ₄	380–450	conductor in IC's	semi- production
TiC	TiCl ₄ -C ₂ H ₂	500	abrasion cutting tools	R & D
TiN	TiCl ₄ -NH ₃	500	abrasion cutting tools	R & D
Diamond-like carbon	CH ₄ -H ₂ hydrocarbon	300	wear, erosion, optical	semi- production

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6

The CVD of Metals

1.0 INTRODUCTION

This and the following chapters are a review of the materials that are deposited by CVD, either on a production basis or experimentally. The listing is not all inclusive as the CVD of many elements and compounds has yet to be investigated or at least adequately reported in the literature. Each material is listed with its basic properties, its major CVD reactions and processes, and its present and potential applications.

Large spreads in the reported values of properties are frequently found in the literature and the testing conditions are often poorly described. In addition to the testing conditions, many other factors may influence the results such as the following:

- Processing conditions (temperature, pressure, etc.).
- Composition and stoichiometry.
- Impurities particularly oxygen and nitrogen.
- Grain size and morphology.
- Grain orientation.
- Structural defects (vacancies, dislocations).
- Presence of different phases.

These factors should be described as much as possible for a test to be meaningful.

The present chapter deals with the CVD of metals and some metal alloys and intermetallics. The metals are listed alphabetically. The range of applications is extensive as many of these materials play an important part in the fabrication of integrated circuits and other semiconductor devices in optoelectronic and optical applications, in corrosion protection, and in the design of structural parts. These applications are reviewed in greater depth in Chs. 13 to 19.

2.0 ALUMINUM

2.1 Characteristics and Properties

Aluminum is a light metal characterized by a low melting point and high electrical conductivity. It has relatively low strength and is highly ductile. Its properties are summarized in Table 6.1.

Table 6.1
Properties of Aluminum at 25°C

Crystal structure: cubic (f.c.c)
Density (g/cm^3): 2.69
Melting point ($^{\circ}\text{C}$): 646
Specific heat ($\text{J}/\text{mol}\cdot\text{K}$): 24.35
Thermal conductivity ($\text{W}/\text{m}\cdot\text{K}$): 237
Thermal expansion ($\times 10^{-6}/^{\circ}\text{C}$): 23.5
Electrical resistivity ($\mu\Omega\cdot\text{cm}$): 2.65

Until recently, aluminum was deposited mostly by evaporation or sputtering, but deposition by MOCVD is becoming popular

because of the better conformal coverage it offers and the CVD of aluminum is becoming an important factor in semiconductor manufacturing. Aluminum is susceptible to electromigration and in integrated circuits this may lead to the formation of spikes that penetrate the silicon junction and cause electrical shorting (see Ch. 12).

2.2 CVD Reactions

The most widely used deposition reaction is the pyrolysis of an aluminum alkyl such as:

- Trimethyl aluminum, $(\text{CH}_3)_3\text{Al}$ or TMA.
- Triethyl aluminum, $(\text{C}_2\text{H}_5)_3\text{Al}$ or TEA.
- Tri-isobutyl aluminum, $(\text{C}_4\text{H}_9)_3\text{Al}$ or TIBA.
- Dimethyl aluminum hydride, $(\text{CH}_3)_2\text{AlH}$ or DMAH.

The decomposition yields the metal and hydrocarbons. The TMA reaction has a tendency to leave carbon incorporated in the metal. Both TEA and TIBA have very low vapor pressure at room temperature and are consequently difficult to use. DMAH is generally the preferred precursor. Deposition temperature range is 200–300°C and pressure up to 1 atm^{[1][2]} (Note: these alkyls are pyrophoric.)

Deposition by the hydrogen reduction of the trihalides (AlX_3) is not practical because of the stability of the latter, but is possible through the disproportionation of the monohalides. This is a difficult procedure which has been largely superseded by the decomposition of the aluminum alkyls mentioned above.^[3]

In addition to these low temperature thermal processes, aluminum can be deposited by the decomposition of an alkyl precursor with a UV laser,^{[4]–[6]} or with an argon-ion laser in applications such as patterns and lithography.^[7] Aluminum has also been deposited at low temperature by magnetron plasma.^[8]

2.3 Applications

- Metallization of semiconductor devices and replacement of evaporated or sputtered films to improve conformal uniformity.^[9]
- Coating of carbon fibers for composite fabrication.
- Corrosion and oxidation protection of steel.
- Alloyed with copper for semiconductor metallization (see Sec. 4.0).

3.0 BERYLLIUM

3.1 Characteristics and Properties

Beryllium is a strong and light metal with useful nuclear characteristics (its atomic number is 4). It oxidizes readily and the oxide is toxic. Its properties are listed in Table 6.2. It is produced by CVD on an experimental basis.

Table 6.2
Properties of Beryllium at 25°C

Crystal structure: hexagonal
Density (g/cm ³): 1.85
Melting point (°C): 1277
Specific heat (J/mol•K): 16.44
Thermal conductivity (W/m•K): 201
Thermal expansion (x 10 ⁻⁶ /°C): 12
Electrical resistivity (μΩ•cm): 4

3.2 CVD Reactions

The beryllium halides are stable compounds and consequently their reduction by hydrogen is not a practical method of obtaining the metal.^[3] Good beryllium deposits are obtained by the pyrolysis of the alkyls as follows:^[10]



The deposition temperature range is 280–305°C and the pressure is <1 Torr. This reaction has a tendency to incorporate carbon in the deposit.

3.3 Applications

- First-wall coatings for fusion reactors.

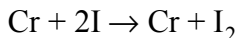
4.0 CHROMIUM

4.1 Characteristics and Properties

Chromium is a hard metal with excellent corrosion and oxidation resistance. Its properties are summarized in Table 6.3. Chromium coatings are usually produced by electroplating or sputtering, but CVD is being investigated for several applications.

4.2 CVD Reactions

Chromium can be deposited by the pyrolysis of the iodide, which is prepared in situ by passing a flow of iodine vapor over the metal at 700°C. The iodide is then decomposed at 1000°C at pressures up to 1 atm as follows:

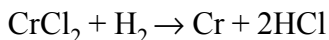


Note: Iodine is mostly monatomic at 1000°C, depending on pressure.

Table 6.3
Properties of Chromium at 25°C

Crystal structure: cubic, body-centered
Density (g/cm ³): 7.20
Melting point (°C): 1865
Specific heat (J/mol•K): 23.29
Thermal conductivity (W/m•K): 91
Thermal expansion (x 10 ⁻⁶ /°C): 6.0
Electrical resistivity (μΩ•cm): 12.9

Chromium can also be prepared by the hydrogen reduction of the chloride at 1200 to 1325°C as follows:^{[3][11][12]}



The MOCVD of chromium is based on the decomposition of dicumene chromium, (C₉H₁₂)₂Cr, at 320–545°C.^{[13][14]} However, the reaction tends to incorporate carbon or hydrogen in the deposit. It can also be deposited by the decomposition of its carbonyl which is made by dissolving the halide in an organic solvent such as tetrahydrofuran with CO at 200–300 atm and at temperatures up to 300°C in the presence of a reducing agent such as an electropositive metal (Na, Al, or Mg), trialkylaluminum, and others.^[3]

4.3 Applications

- Corrosion protection and oxidation protection of steels and other metals.
- Experimental contact metallization in integrated electronic circuits.

5.0 COPPER

5.1 Characteristics and Properties

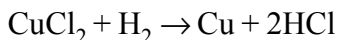
Copper is a malleable and ductile metal with high thermal conductivity. It is an excellent electrical conductor which, unlike aluminum, is not readily susceptible to electromigration. It is generally produced by electroplating or sputtering, but CVD processing is being investigated to deposit electrical conductors in semiconductor applications to replace aluminum (see Ch. 12). Its properties are summarized in Table 6.4.

Table 6.4
Properties of Copper at 25°C

Crystal structure: cubic (f.c.c)
Density (g/cm^3): 8.96
Melting point ($^{\circ}\text{C}$): 1083
Specific heat ($\text{J}/\text{mol}\cdot\text{K}$): 24.33
Thermal conductivity ($\text{W}/\text{m}\cdot\text{K}$): 385
Thermal expansion ($\times 10^{-6}/^{\circ}\text{C}$): 16.6
Electrical resistivity ($\mu\Omega\cdot\text{cm}$): 1.673

5.2 CVD Reactions

Deposition can be carried out by the hydrogen reduction of the chloride at high temperature (up to 1000°C):



Deposition occurs at much lower temperature (260–340°C) by the decomposition of metallo-organic compounds such as copper acetylacetonate, $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$, or by the hydrogen reduction of the copper chelate, $\text{Cu}(\text{C}_5\text{HF}_6\text{O}_2)_2$ at 250°C^{[15][16]} and more recently of copper (I) β -diketonate compounds or from copper hexafluoroacetylacetonate which proceed at low deposition temperatures (ca. 200°C) and have high deposition rates (ca. 900 nm/min).^{[15]–[17]}

5.3 Applications

- Conductive coatings for semiconductor applications.
[17]
- Alloying element with CVD aluminum to reduce electromigration.

6.0 GOLD

6.1 Characteristics and Properties

Gold is an extremely malleable and ductile precious metal with excellent corrosion and oxidation resistance. Its properties are summarized in Table 6.5.

It is generally deposited by electroplating or sputtering but its CVD is being considered in semiconductor applications.

Table 6.5
Properties of Gold at 25°C

Crystal structure: cubic (f.c.c)
Density (g/cm ³): 18.8
Melting point (°C): 1064
Specific heat (J/mol•K): 25.31
Thermal conductivity (W/m•K): 315
Thermal expansion ($\times 10^{-6}/^{\circ}\text{C}$): 14.2
Electrical resistivity ($\mu\Omega\cdot\text{cm}$): 2.35
Hall constant ($10^{-4}\text{ cm}^3/\text{A}\cdot\text{s}$):

6.2 CVD Reactions

Since gold has a relatively low melting point, high-temperature reactions are not possible. It is deposited by the decomposition of metallo-organics such as the following:^[18]

- Dimethyl 1-2,4 pentadionate gold (III).
- Dimethyl- (1,1,1-trifluoro-2-4-pentadionate) gold (III).
- Dimethyl- (1,1,1-5,5,5 hexafluoro 2-4 pentadionate) gold (III).

In addition to thermal MOCVD, laser CVD has been successfully demonstrated.^{[19][20]}

6.3 Applications

- Contact metallization and metallization of alumina in semiconductor applications.

7.0 MOLYBDENUM

7.1 Characteristics and Properties

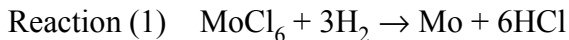
Molybdenum is a high-strength refractory metal, although recrystallizes above 950°C with accompanying reduction in mechanical properties. It is easily fabricated. Its properties are summarized in Table 6.6. CVD is commonly used for the production of molybdenum coatings and free-standing shapes.

Table 6.6
Properties of Molybdenum at 25°C

Crystal structure: cubic, body-centered
Density (g/cm ³): 10.22
Melting point (°C): 2620
Specific heat (J/mol•K): 24.23
Thermal conductivity (W/m•K): 138
Thermal expansion (x 10 ⁻⁶ /°C): 5.0
Electrical resistivity (μΩ•cm): 15.4
Hall constant (10 ⁻⁴ cm ³ /A•s):

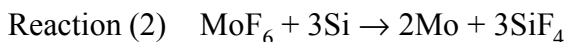
7.2 CVD Reactions

The hydrogen reduction of the chloride is the most commonly used deposition reaction:^[3]



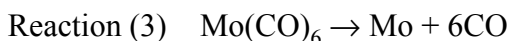
This reaction has a $\Delta G^\circ = -114$ Kcal/mole Mo at 800K and it occurs over a wide range of temperature (400–1350°C). Best deposits are obtained at low pressure (<20 Torr) and at the high end of the temperature range. The reaction is used in the production of metallurgical coatings.

Another common reaction is the silicon reduction of the fluoride:



This reaction has a $\Delta G^\circ = -162$ Kcal/mole Mo at 800K. Deposition temperature is 200–500°C at low pressures (<20 Torr). MoF_6 tends to decompose into F_2 and solid MoF_3 which results in inconsistency in the coating especially at temperatures <400°C. This reaction, which has been considered for the metallization of IC's, is now largely superseded by tungsten deposition.^{[21][22]}

Another well-established metallization reaction is the decomposition of the carbonyl:



Reaction temperature ranges from 300 to 700°C and pressure from about 1 Torr to 1 atm. The reaction is carried out in a hydrogen atmosphere to reduce the possibility of carbon contamination. A deposition temperature > 450°C is required to eliminate the incorporation of C and O_2 in the deposit.^{[23]–[25]}

In addition to the thermal CVD systems mentioned above, molybdenum is deposited by plasma CVD using Reaction (3) in hydrogen.^[26] Annealing is required to remove incorporated carbon and oxygen.

7.3 Applications

- IC's contact and gate metallization using Reaction (3).
- Schottky contact metallization.
- Erosion resistant coatings for gun steel barrels deposited with carbonyl precursor.^[27]
- Coatings for photothermal solar converters with high infrared reflectance, which use Reaction (3) and a 1000°C anneal.^[28]
- Coatings for high power laser mirrors using Reaction (3) and thermal annealing.^[29]
- Freestanding shapes such as tubes and rods.

8.0 NICKEL

8.1 Characteristics and Properties

Nickel is a ductile, malleable and ferromagnetic metal. Its properties are summarized in Table 6.7.

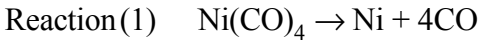
Table 6.7
Properties of Nickel at 25°C

Crystal structure: cubic (f.c.c)
Density (g/cm ³): 8.98
Melting point (°C): 1453
Specific heat (J/mol•K): 26.07
Thermal conductivity (W/m•K): 90
Thermal expansion (x 10 ⁻⁶ /°C): 13
Electrical resistivity (μΩ•cm): 6.84
Hall constant (10 ⁻⁴ cm ³ /A•s):

Nickel coatings are mostly produced by electroplating, but CVD nickel is gaining in importance.

8.2 CVD Reactions

The most commonly used reaction is the decomposition of nickel carbonyl:

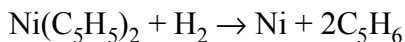


This reaction can occur over a temperature range of 150–200°C with optimum temperature of 180–200°C. Pressure is up to 1 atm (see Ch. 3, Sec. 4.2). A partial pressure of CO inhibits the reaction. Above 200°C, carbon tends to deposit together with the nickel. The reaction can be catalyzed by hydrogen sulfide and deposition can be obtained as low as 100°C.^{[3][30][31]} More ductile nickel is obtained at low deposition rates (note: nickel carbonyl is highly toxic). Ni(CO)₄ is obtained by reacting finely divided nickel powder with CO. This reaction proceeds at atmospheric pressure and at temperatures between 45 and 90°C with optimum temperature of 80°C. It occurs in two steps as follows:



This is the Mond reaction, first developed by Ludwig Mond in 1890. It is still used for the production and purification of metallic nickel. A similar reaction is used for the production of Fe(CO)₅ but higher temperature is required.

Nickel is also deposited from the alkyl at 200°C as follows:^[32]



It can also be deposited by the hydrogen reduction of the nickel chelate, $\text{Ni}(\text{C}_5\text{HF}_6\text{O}_2)_2$ at 250°C .^[33] In addition to thermal processing reviewed above, nickel is deposited by laser CVD from the carbonyl with a krypton or a pulsed CO_2 laser.^{[34][35]}

8.3 Applications

- Molds, dies, and other forming tools for metal and plastic processing, especially those involving irregular surfaces and internal areas.
- High strength structural parts when alloyed with small amounts of boron (0.05–0.2 wt.%) produced by codeposition from $\text{Ni}(\text{CO})_4$ and B_2H_6 .^[36]
- Contacts for electronic applications (alloyed with palladium).

9.0 NIOBIUM (COLUMBIUM)

9.1 Characteristics and Properties

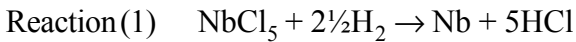
Niobium (also known as columbium) is a soft, ductile, refractory metal with good strength retention at high temperature, and a low capture cross-section for thermal neutrons. It is readily attacked by oxygen and other elements above 200°C . CVD is used to produce coatings or free standing shapes. The properties of niobium are summarized in Table 6.8.

Table 6.8
Properties of Niobium at 25°C

Cubic structure: cubic (b.c.c)
Density (g/cm ³): 8.57
Melting point (°C): 2468
Specific heat (J/mol•K): 24.43
Thermal conductivity (W/m•K): 52
Thermal expansion (x 10 ⁻⁶ /°C): 7
Electrical resistivity (μΩ•cm): 12.5
Hall constant (10 ⁻⁴ cm ³ /A•s): +0.9

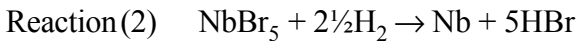
9.2 CVD Reactions

Niobium is generally deposited by the hydrogen reduction of its chloride which is accomplished at 900–1300°C and at pressure up to 1 atm as follows:



The chloride is usually prepared by direct chlorination in situ by heating the metal chips to 300°C (see Ch. 4, Sec. 3.1).

Deposition is also feasible by the hydrogen reduction of the bromide at 1200°C as follows:



If a graphite substrate is used, Reaction (2) produces niobium carbide which may remain incorporated in the metal deposit.^[37] Niobium absorbs hydrogen readily and, for that reason, an inert atmosphere such as argon is used in the heating and cooling cycles.

9.3 Applications

- Coatings for nuclear fuel particles.
- Cladding for steel and copper tubing for chemical processes.

10.0 PLATINUM AND PLATINUM GROUP METALS

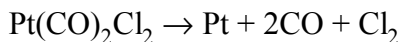
10.1 Characteristics and Properties

The platinum-group metals comprise ruthenium (Ru), rhodium (Rh) and palladium (Pd) from the second transition series and osmium (Os), iridium (Ir), and platinum (Pt) from the third transition series. Little or no CVD investigation of palladium and osmium have been reported and these metals are not included here. The properties of the other platinum-group metals are summarized in Table 6.9.

10.2 Platinum

Pure platinum is malleable and ductile with excellent corrosion resistance. When alloyed with cobalt, it has good magnetic properties (76.7 W% Pt, 23.3 W% Co).

CVD Reactions. The platinum halides are volatile with a decomposition point too close to the vaporization point to make them practical for CVD transport.^[3] Platinum can be deposited by the decomposition of the acetylacetonate, although carbonaceous impurities remain in the deposit. The carbonyl halides, specifically dicarbonyl dichloride, are more satisfactory precursors. The decomposition reaction is as follows:



Reaction temperature range is 500–600°C. The carbonyl partial pressure is 10–20 Torr. [38]

Table 6.9
Properties of Platinum-Group Metals at 25°C

	Platinum	Iridium	Rhodium	Ruthenium
Crystal structure:	f.c.c	f.c.c	f.c.c	f.c.c
Density (g/cm ³):	21.4	22.5	12.4	12.2
Melting point (°C):	1772	2410	1963	2250
Specific heat (J/mol•K):	25.06	24.97	24.97	24.05
Thermal conductivity (W/m•K):	71	147	150	117
Thermal expansion (x 10 ⁻⁶ /°C):	8.8	6.4	6.2	6.4
Electrical resistivity (μΩcm):	10.6	5.4	4.5	7.6

Platinum produced by the decomposition of platinum hexafluoro-2,4-pentadionate, $\text{Pt}(\text{CF}_3\text{COCHCOCF}_3)_2$, by an argon laser has been reported. [39] The metal can also be obtained from the decomposition of tetrakis-trifluorophosphine, $\text{Pt}(\text{PF}_3)_4$ at 200–300°C in an atmosphere of hydrogen. [38]

10.3 Applications

- Coatings for high temperature crucibles.
- Catalyst in fuel cells and automobile emission control.

- Ohmic and Schottky diode contacts.
- Diffusion barrier metallization.

10.4 Iridium

Iridium is the most corrosion and oxidation resistant metal and the densest element after osmium. It is hard and brittle and as such it is difficult to machine or form. This limitation has spurred the development of vapor deposition.

CVD Reactions. The hydrogen reduction of the fluoride (IrF_6) does not produce a satisfactory coating.^[40] A common deposition reaction is the pyrolysis of the acetyl acetonate, $\text{Ir}(\text{CH}_3\text{COCHCOCH}_3)_3$ which can be vaporized in a fluidized bed at 235°C . Deposition temperature range is $400\text{--}450^\circ\text{C}$ and pressure is 1 atm. Carbon tends to be incorporated in the deposit above these temperatures.^{[41][42]} With the proper conditions, high quality, dense deposits are obtained by this method.

10.5 Applications

- Corrosion resistant and oxidation resistant coatings for rocket engines and other aerospace applications.
- Coatings for thermionic cathodes.

10.6 Rhodium and Ruthenium

Rhodium is a hard metal with high reflectance and good resistance to corrosion. Ruthenium has properties which are similar to those of rhodium.^[43] The CVD of both metals is similar.

CVD Reactions. The rhodium halides, like those of the other platinum group metals, are volatile with a decomposition point too close to the vaporization point to make them usable for CVD transport. The metal is commonly produced by the decomposition of metallo-organic precur-

sors such as rhodium acetyl acetate, $\text{Rh}(\text{CH}_3\text{COCHCOCH}_3)_3$. This precursor evaporates at 230°C and the metal is deposited at 250°C and at 1 atm pressure. Another precursor is rhodium trifluoro-acetyl acetate, $\text{Rh}(\text{C}_5\text{H}_4\text{F}_3\text{O}_2)_3$. The reaction takes place at 400°C and at 1 atm pressure.^[44]

Rhodium is also produced by the decomposition of the carbonyl, $\text{Rh}_4(\text{CO})_{12}$, at temperatures above 95°C , the metal being deposited at approximately 250°C .^{[42][45]}

11.0 RHENIUM

11.1 Characteristics and Properties

Rhenium has a high melting point, second only to tungsten among the metals. It has a high modulus of elasticity and it maintains its h.c.p. crystal structure to its melting point. It has a high rate of work hardening. Annealed rhenium is remarkably ductile and can be bent, coiled or rolled. At elevated temperature, its ultimate tensile strength is considerably higher than that of the other refractory metals, including tungsten, and is still appreciable above 2000°C .^[46]

Rhenium has good chemical resistance due to its position in the periodic table next to the noble metals of the platinum group. However, it oxidizes readily. Its properties are summarized in Table 6.10.

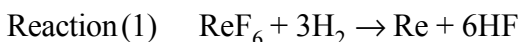
Rhenium is highly refractory and difficult and costly to process by standard metallurgical practices. However, it is produced readily by CVD.

Table 6.10
Properties of Rhenium at 25°C

Crystal structure: h.c.p.
Density (g/cm ³): 21.0
Melting point (°C): 3180
Specific heat (J/mol•K): 25.31
Thermal conductivity (W/m•K): 48
Thermal expansion (x 10 ⁻⁶ /°C): 6.7
Electrical resistivity (μΩ•cm): 19.3
Hall constant (10 ⁻⁴ cm ³ /A•s):

11.2 CVD Reactions

Rhenium is generally deposited by either the hydrogen reduction or by the thermal decomposition of its halides.^[48] The structure of the rhenium atom is such that it possesses all valence states from Re⁻¹ to Re⁺⁷ of which Re⁺⁷ is the strongest and characteristic valence. This multivalence results in the formation of a wide series of halides and at least three fluorides and up to six chlorides have been identified. However, with these halides, the maximum valence state of 7 is never realized, probably due to the fact that the rhenium atom is not capable of accommodating 7 atoms of the halogen. The hydrogen reduction of the fluoride is as follows:



Deposition temperature range is 500–900°C with best deposits obtained at 700°C. At the low end of the temperature range, fluoride compounds remain incorporated in the deposit. Pressure is usually < 20

Torr. Reaction (1) is a simplified version of a reaction that involves the formation of subfluorides such as ReF_4 . Grain refinement is obtained by the addition of a small amount of H_2O in the gas stream.^[48] The hydrogen reduction of the chloride is not normally used since it produces gas phase precipitation which is almost impossible to avoid.

Another CVD reaction is the pyrolysis of the chloride:



Deposition temperature range is 1000–1250°C and best deposits are obtained at low pressure (<20 Torr). This reaction usually gives a more ductile and purer material than does Reaction (1) although higher temperature is necessary. The chloride is generally prepared in situ by direct chlorination by heating the metal at 500–600°C (see Ch. 4).^[3]

Rhenium can also be deposited by the pyrolysis of the carbonyl:



Deposition temperature range is 400–600°C at a pressure of 200 Torr. Rhenium carbonyl is a solid at room temperature and must be vaporized at a temperature > 117°C. It decomposes at 250°C. This reaction is used for the coating of spheres in a fluidized bed.^[49]

11.3 Applications

- Heaters for high temperature furnaces.
- Boats, crucibles, tubes, and other freestanding shapes.
- Contacts and diffusion-barrier metallization and selective deposition on silicon in semiconductor applications (experimental).
- Thermocouple sheaths.

12.0 TANTALUM

12.1 Characteristics and Properties

Tantalum is a refractory metal with a high melting point and excellent chemical resistance, especially to acid corrosion. It is ductile when pure. Its properties are summarized in Table 6.11.^[50] It is readily produced by CVD.

Table 6.11
Properties of Tantalum at 25°C

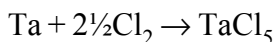
Crystal structure: b.c.c
Density (g/cm³): 16.65
Melting point (°C): 2996

Specific heat (J/mol•K): 25.35
Thermal conductivity (W/m•K): 54
Thermal expansion (x 10⁻⁶/°C): 6.5

Electrical resistivity (μΩ•cm): 12.45
Hall constant (10⁻⁴ cm³/A•s):

12.2 CVD Reactions

The direct decomposition of the chlorides is readily accomplished but requires high temperatures. For that reason hydrogen reduction is preferable.^{[51][52]} The chloride is generated in situ (see Ch. 4) at 550°C as follows:



This reaction occurs in the temperature range of 900–1300°C at low pressure (ca. 10 Torr). Tantalum has a high affinity for hydrogen and, for that reason, it is preferable to heat and cool the reactor in an inert atmosphere such as argon. The hydrogen reduction of the bromide or iodide is also feasible but is used less frequently.

12.3 Applications

- Thin film capacitors.
- Corrosion resistant coatings.
- Ordnance devices.

13.0 TITANIUM

13.1 Characteristics and Properties

Titanium is a light metal with high strength and excellent corrosion resistance. It is readily produced by CVD and has important applications, particularly in semiconductors. Its properties are summarized in Table 6.12

Table 6.12
Properties of Titanium at 25°C

Crystal structure: hexagonal (α), changes to cubic in a sluggish transformation at 800°C

Density (g/cm^3): 4.54

Melting point ($^{\circ}\text{C}$): 1660

Specific heat ($\text{J}/\text{mol}\cdot\text{K}$): 25.05

Thermal conductivity ($\text{W}/\text{m}\cdot\text{K}$): 21.9

Thermal expansion ($\times 10^{-6}/^{\circ}\text{C}$): 8.5

Electrical resistivity ($\mu\Omega\cdot\text{cm}$): 43

Hall constant ($10^{-4}\text{ cm}^3/\text{A}\cdot\text{s}$): -0.2

Magnetic susceptibility (10^{-6} emu/mol):

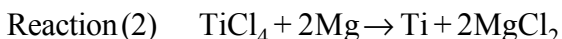
13.2 CVD Reactions

The thermal decomposition of the iodide or bromide is used to deposit titanium in the temperature range of 1200–1500°C as follows:



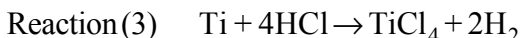
Note: iodine is monatomic at these temperatures

The magnesium reduction is used extensively in the industrial production of the metal as follows:



This reaction cannot be considered as a controlled CVD reaction although some CVD mechanisms may be involved. A possible mechanism would be the reaction of TiCl_4 gas with solid or molten Mg, and then with Mg dissolved in liquid MgCl_2 .

A common CVD reaction is the hydrogen reduction of the tetrachloride, TiCl_4 , which is liquid at room temperature. It is transported into the reactor by a stream of hydrogen or else is prepared in situ by passing HCl, highly diluted with H_2 , over titanium chips heated at 750–800°C. The chlorination reaction is as follows:



Deposition of the titanium probably occurs by the disproportionation of the lower chlorides in an essentially inert hydrogen, followed by the hydrogen reduction of the subchloride. Titanium readily absorbs hydrogen interstitially to form titanium hydride (TiH_2). This would be detrimental to the properties of the coating and should be avoided by cooling; in an inert atmosphere such as argon after the reaction is completed. This hydrogen reduction of the chloride is promoted when it occurs in a plasma.^[53]

Titanium can also be produced by the thermal decomposition of metallo-organics such as tris-(2,2'-bipyridine) titanium at $< 600^{\circ}\text{C}$. The deposit tends to retain impurities such as C, N_2 , and H_2 .^{[53][54]}

13.3 Applications

- Production of metal foils and shapes.
- Corrosion resistant coatings on steel and other substrates.
- Preparation of titanium aluminides.
- Diffusion barrier in semiconductors.

14.0 TUNGSTEN

14.1 Characteristics and Properties

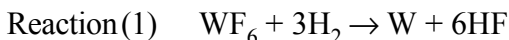
Tungsten is a highly refractory, high-density metal. It has excellent chemical resistance except that it oxidizes readily. It is brittle mostly because of impurities and is difficult to form by standard metallurgical processes. It can be produced easily by CVD as a very pure and relatively ductile metal. CVD tungsten is used in many applications and is an important semiconductor metal. Its properties are summarized in Table 6.13.

Table 6.13
Properties of Tungsten at 25°C

Crystal structure: cubic, body-centered (b.c.c)
Density (g/cm^3): 19.3
Melting point ($^{\circ}\text{C}$): 3410
Specific heat ($\text{J}/\text{mol}\cdot\text{K}$): 24.3
Thermal conductivity ($\text{W}/\text{m}\cdot\text{K}$): 173
Thermal expansion ($\times 10^{-6}/^{\circ}\text{C}$): 4.5
Electrical resistivity ($\mu\Omega\cdot\text{cm}$): 5.65
Hall constant ($10^{-4} \text{ cm}^3/\text{A}\cdot\text{s}$):

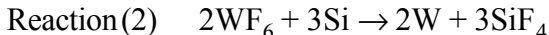
14.2 CVD Reactions

Tungsten is usually obtained by the hydrogen reduction of the fluoride as follows:



This reaction has a $\Delta G = -33$ Kcal/mol at 800K and an activation energy of 67 KJ/mol. The deposition temperature range is 300–700°C and the pressure ranges from 10 Torr to 1 atm. Above 450°C, the reaction is diffusion controlled and relatively insensitive to temperature. Lower temperature (500°C) gives a finer grain structure with high strength (83 MPa) than high temperature (700°C). Grain refinement is obtained with alternate deposition of silicon (see Ch. 2). This reaction is used extensively in semiconductor applications.^[55] A typical apparatus for blanket and integrated deposition is completely automated.^[56]

Another deposition reaction is the silicon reduction of the fluoride:



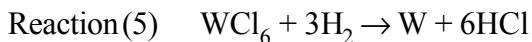
This reaction has a $\Delta G = -153$ Kcal/mol W @ 800K. The deposition temperature range is 310–540°C and the pressure range 1–20 Torr. It is normally used on a silicon wafer substrate which becomes the source of silicon. It is self-limiting since it depends on the diffusion of WF_6 through the tungsten layer which can reach a maximum thickness of approximately one micron.^{[57][58]} Reaction (2) has a much greater driving force than Reaction (1) and will always occur first.

The selective deposition of tungsten can be obtained with the following reactions:^[59]



In contrast with Reaction (3), Reaction (4) is not strongly affected by the nature of substrate which can be tungsten or silica.

Another deposition reaction is the hydrogen reduction of the chloride as follows:



This reaction has a $\Delta G = -108$ Kcal/mol W at 800K. The deposition temperature range is 900–1300°C and the pressure range: 15–20 Torr. The reaction produces high purity deposits and is used to coat x-ray targets and produce structural parts. WCl_6 can be obtained by the direct chlorination in situ of the metal (see Ch. 4).

Tungsten can also be obtained by the pyrolysis of the carbonyl as follows:



The deposition temperature range is 250–600°C and the pressure is up to 20 Torr. To minimize carbon inclusion, the carbonyl is highly diluted with hydrogen (ratio of 1/100) and high purity deposits can be obtained.^[3] Reaction (6) has a low temperature reaction and is being considered for deposition on silicon and III–V semiconductors.

In addition to the thermal CVD reactions listed above, tungsten can be deposited by plasma CVD using Reaction (1) at 350°C.^{[60][61]} At this temperature, a metastable alpha structure (αW) is formed instead of the stable b.c.c. Tungsten is also deposited by an excimer laser by Reaction (1) at < 1 Torr to produce stripes on silicon substrate.^[62]

14.3 Applications

- Replacement of aluminum and general metallization of integrated circuits (IC's).

- Selective deposition, via plugs and gate electrodes for very large scale integrated circuits (VLSI).
- Diffusion barriers between silicon and aluminum in IC's.
- Thermionic cathodes (co-deposited with thorium).^[63]
- Coating for targets for x-ray cathodes (co-deposition with rhenium).
- Selective absorber coatings for solar energy collectors.^[64]

15.0 OTHER METALS

In addition to the metals mentioned above, the CVD of a number of other metals has been reported. The CVD of these metals is of minor importance, at least so far, and is only summarized here.

15.1 Cadmium

Cadmium is a toxic, soft metal with good corrosion resistance, low melting point (321°C) and high thermal expansion (30 ppm/°C at 25°C). It has an hexagonal structure, a thermal conductivity of 0.91 W/cm•°C at 25°C and an electrical resistivity of 6.83 μohm-cm at 20°C. It is normally deposited by electroplating and its processing by CVD has been accomplished by thermal-laser CVD using the decomposition of dimethyl cadmium, $\text{Cd}(\text{CH}_3)_2$, at 10 Torr with an argon laser.^[65]

15.2 Iron

Iron is very reactive chemically and oxidizes readily. It has four allotropic forms, one of which (α) is magnetic with a Curie transition point of 770°C. It has a density of 7.6 g/cm³, a melting point of 1536°C, a thermal expansion of 12.6 ppm/°C at 25°C, a thermal conductivity of 0.80 W/cm•°C at 25°C and an electrical resistivity of 9.71 μohm-cm at 20°C.

Iron has been deposited by the hydrogen reduction of its chloride at 650°C or the pyrolysis of its iodide at 1100°C, as well as the decomposition of its carbonyl at 370–450°C with CO as carrier gas. Carbon tends to be incorporated in the deposit requiring a 900°C annealing in H₂ to remove it.^{[3][66]} A potential application is epitaxial films on GaAs.

15.3 Tin

The common white tin (β -Sn) has a tetragonal structure, a density of 7.3 g/cm³ and a low melting point of 232°C. It is generally chemically inert and oxidation resistant. It has a thermal expansion of 20 ppm/°C at 25°C, a thermal conductivity of 0.6 W/cm•°C at 25°C and an electrical resistivity of 11 μ ohm-cm at 0°C.

Tin is deposited by CVD on an experimental basis, but because it must be deposited above its melting point, no practical applications are known at this time. The hydrogen reduction of the chloride (SnCl₂) produces tin at 400–500°C.^[67] It is also deposited from the alkyls, such as the tetramethyl or triethyl tin, Sn(CH₃)₄, Sn₂(C₂H₅)₃ at 500–600°C and usually low pressure.^[68]

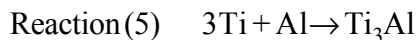
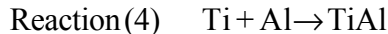
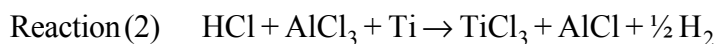
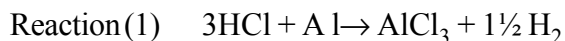
16.0 INTERMETALLICS

Intermetallics are compounds of two metals in which a progressive change in composition is accompanied by a progression of phases with different crystal structure. Many intermetallics have high strength at high temperature, high stiffness, and low density. Their limitations are generally low room temperature ductility and low fracture toughness. Some of the most important intermetallics are the aluminides of titanium, nickel, and iron. Several intermetallics have been produced by CVD on an experimental basis. The most important are listed below.

16.1 Titanium Aluminides

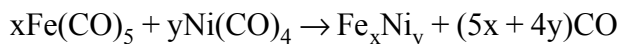
There are two important titanium aluminides: Ti_3Al which has a hexagonal structure with a density of 4.20 g/cm^3 and a melting point of 1600°C and TiAl which has a tetragonal structure with a density of 3.91 g/cm^3 and a melting point of 1445°C . As do all aluminides, they have excellent high temperature oxidation resistance owing to the formation of a thin alumina layer on the surface. They have potential applications in aerospace structures.^[69]

Titanium aluminides are produced by CVD from the halides by the following sequence of reactions:^[70]



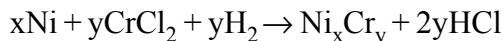
16.2 Ferro-Nickel

Ferro-nickel is produced by the co-decomposition of the carbonyl as follows:^[71]



16.3 Nickel-Chromium

Nickel-chromium is produced by reaction of CrCl_2 with a nickel surface in a hydrogen atmosphere as follows:^[72]

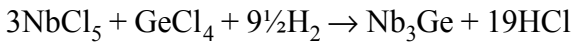


16.4 Tungsten-Thorium

Tungsten-thorium intermetallics are used as a long life thermionic cathode emitter for high-power applications in high-frequency tubes. They are obtained by CVD from tungsten fluoride and a thorium metallo-organic such as thorium hepta-fluorodimethyl octanedione, $\text{Th}(\text{C}_{10}\text{H}_{10}\text{F}_7\text{O}_2)_4$ in a codeposition reaction at 800°C and 10–100 Torr.^[63]

16.5 Niobium-Germanium

Niobium germanide, Nb_3Ge , is a superconductor with a high transition temperature ($T_c = 20\text{K}$). It is prepared by CVD by the co-reduction of the chlorides as follows:



The chlorides are prepared in situ and the deposition reaction temperature is 900°C.^{[73][74]}

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The CVD of the Allotropes of Carbon

1.0 THE ALLOTROPES OF CARBON

The carbon atom has four valence electrons and four vacancies in its outer shell with a ground state electron configuration of $1s^2 2s^2 2p^2$. Such a configuration allows the ready formation of several allotropic forms: graphite, microcrystalline carbon, diamond, lonsdaleite (a form detected in meteorites), and the recently discovered 60-atom (or more) carbon spherical molecule, the so-called fullerenes.^[1] These allotropes (or polymorphs) have the same building block, the carbon atom, but their physical form – the way the building blocks are put together, i.e., their crystalline structure – is different. Carbon is unique among all the elements in the number and the variety of its allotropes.

This chapter is a review of the two major allotropes: graphite and diamond, which are both produced extensively by CVD. The properties of these two materials can vary widely. For instance, diamond is by far the hardest-known material, while graphite can be one of the softest. Diamond is transparent to the visible spectrum, while graphite is opaque; diamond is an electrical insulator, while graphite is a conductor.

2.0 THE CVD OF GRAPHITE

2.1 Structure of Graphite

The structure of graphite is shown in Fig. 7.1. The carbon atoms form continuous hexagons in stacked basal planes (ab direction). Within each basal plane, the carbon atom is strongly bonded to its three neighbors with a covalent bond, having a bond strength of 524 KJ/mol. This atomic bonding is threefold coordinated and is known as sp^2 . The hybridized fourth valence electron is bonded to an electron of the adjacent plane by a much weaker metallic-like bond of only 7 KJ/mol. The spacing between basal planes (0.335 nm) is larger than the spacing between atoms in the plane (0.142 nm). Such a configuration results in a large anisotropy in the crystal which, in turn, results in a large anisotropy of the properties.

Graphite is commonly produced by CVD and is often referred to as pyrolytic graphite. It is an aggregate of graphite crystallites, which have dimensions (L_c) that may reach several hundred nm. It has a turbostratic structure, usually with many warped basal planes, lattice defects, and crystallite imperfections. Within the aggregate, the crystallites have various degrees of orientation. When they are essentially parallel to each other, the nature and the properties of the deposit closely match that of the ideal graphite crystal.^{[1][2]}

2.2 Properties of CVD Graphite

The properties of CVD graphite are similar to these of single crystal graphite. It is a highly refractory material, which is practically unaffected by thermal shock. It is very inert to most chemical environments except oxygen and it oxidizes readily above 500°C. Its properties are summarized in Table 7.1.^{[3]–[6]} The spread in value may represent slightly different materials and differences in the degree of graphitization and may also reflect variations in the test methods. These values reflect the large anisotropy of the properties.

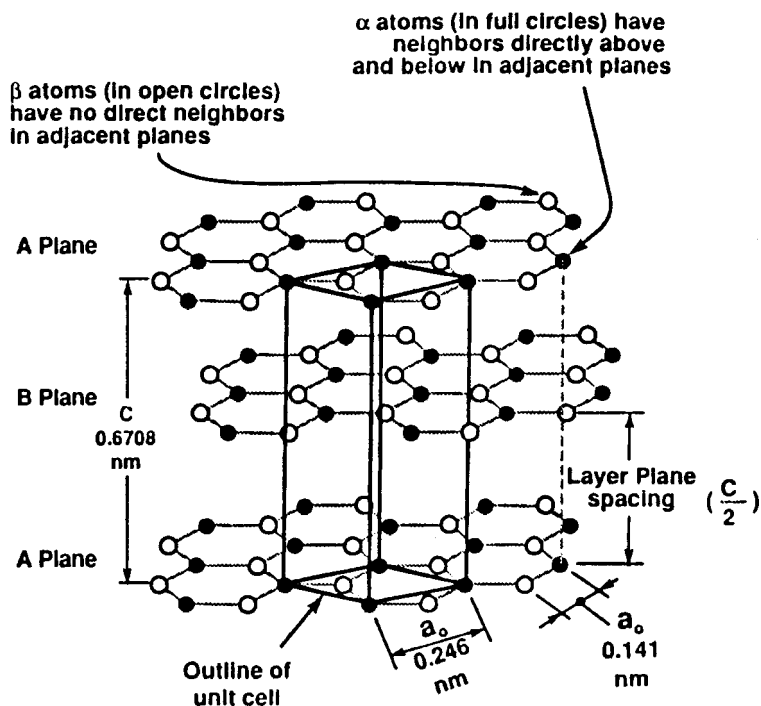


Figure 7.1. Structure of graphite.

2.3 The CVD of Graphite

The CVD of graphite is theoretically simple and is based on the thermal decomposition (pyrolysis) of a hydrocarbon gas. The actual mechanism of decomposition, however, is complex and still not completely understood. This may be due, in part, to the fact that most of the studies on the subject of hydrocarbon decomposition are focused on the improvement of fuel efficiency and the prevention of carbon formation (e.g., soot), rather than the deposition of a coating.

Table 7.1
Properties of CVD Graphite at 25°C

Crystalline form: hexagonal
Lattice parameters: $a_o = 0.246$ nm, $c_o = 0.671$ nm
Color: Black
Sublimation point at 1 atm (estimated): 4000 K
Density, g/cm ³ : 2.10–2.24
Flexural strength (c direction), MPa: 80–170
Tensile strength (ab direction), MPa: 110
Young's modulus of elasticity, GPa: 28–31
Thermal conductivity, W/m•K:
c direction: 1–3
ab directions: 190–390
Thermal expansion 0–100°C, $\text{m} \times 10^{-6}/\text{m} \cdot \text{K}$:
c direction: 15–25
ab direction: -1 to 1
Electrical resistivity, $\mu\Omega\text{m}$: c direction: 1000–3000
ab directions: 4–5

The most common precursor is methane (CH_4), which is generally pyrolyzed at 1100°C or above, over a wide range of pressure from about 100 Pa (0.001 atm) to 10^5 Pa (1 atm). The reaction in a simplified form is as follows:^{[7][8]}



Other common precursors are ethylene (C_2H_6) and acetylene (C_2H_2). Acetylene can also be decomposed at lower temperatures (300–750°C) and at pressures up to 1 atm, in the presence of a nickel catalyst.^[9] Another common precursor is propylene (C_3H_6), which decomposes in the 1000–1400°C temperature range at low pressure ($\approx 1.3 \times 10^4$ Pa or 100 Torr).^[10]

The activation energies for the decomposition of these precursor gases still are not accurately known and show a large scatter. Some reported values are as follows:

- Methane, 78–106 kcal/g•mole.
- Ethane, 60–86 kcal/g•mole.
- Acetylene, 30–50 kcal/g•mole.

2.4 Deposition Mechanism

The pyrolysis of a hydrocarbon, such as shown in Reaction (1), is actually a series of more complex reactions involving molecules of gradually increasing size. A spectrographic analysis of the by-products of the decomposition of methane revealed the presence of large amounts of acetylene, ethylene, and benzene, plus a variety of compounds consisting mostly of the polyaromatic hydrocarbons (PAH), such as naphthalene, anthracene, phenantrene, acenaphthylene, pyrene, and fluoranthene, in addition to the deposited pyrolytic graphite. Some of these compounds form the soot and tarry deposits, which are often observed on the wall of CVD reactors during carbon deposition. The following simplified deposition sequence is probably taking place: methane \rightarrow benzene \rightarrow polyaromatic hydrocarbons \rightarrow carbon.^[7]

2.5 Structural Features of CVD Graphite

CVD graphite can have several structural forms: columnar, laminar, or isotropic. The columnar form is shown in Fig. 7.2. The crystallites are deposited with the basal planes (ab directions) essentially parallel to the deposition surface. Their structure tends to be columnar (cone-like) as a result of uninterrupted grain growth toward the reactant source.

The laminar form consists of essentially parallel layers or concentric shells if deposited on a particle or fiber as shown in Fig.

7.3. Both columnar and laminar structures are optically active to polarized light and usually have similar physical properties.^{[1][2][8]}

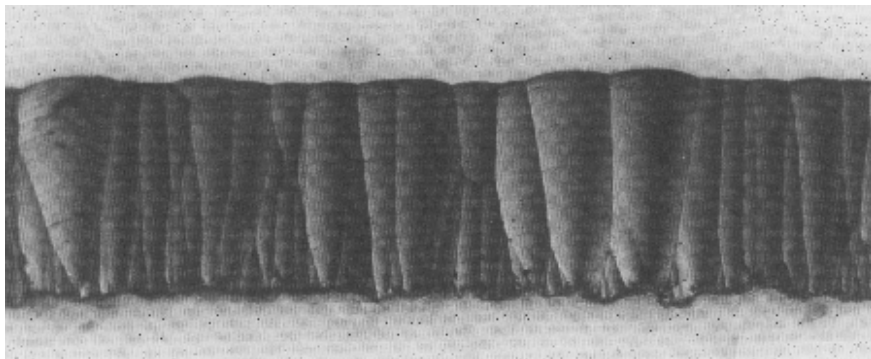


Figure 7.2. Columnar structure of pyrolytic graphite.

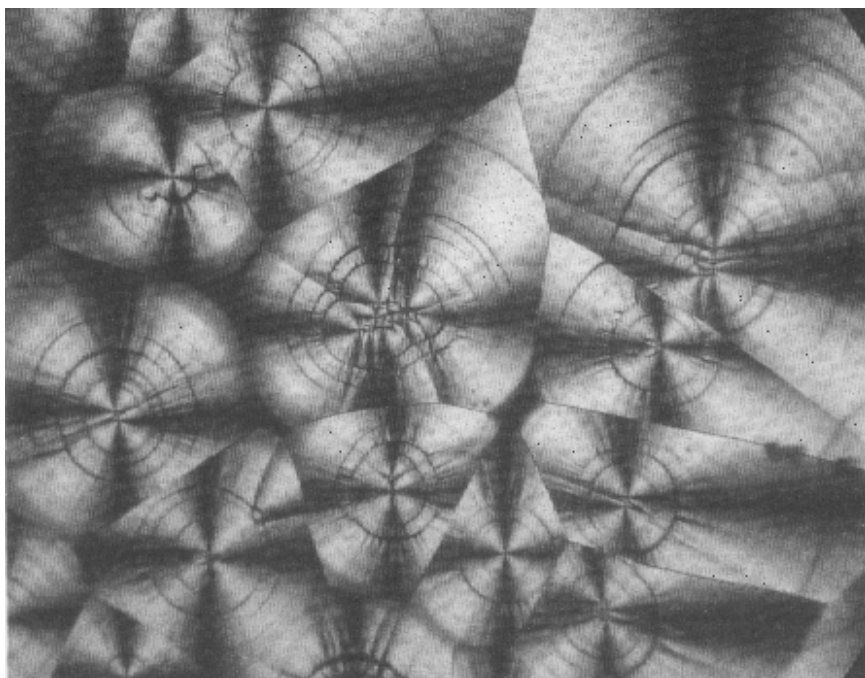


Figure 7.3. Laminar structure of pyrolytic graphite. (Photograph Courtesy of Jack Chin, La Costa CA)

The isotropic form has little graphitic characteristic and essentially no optical activity. It is composed of very fine grains without observable orientation and for this reason, it is known as isotropic carbon rather than isotropic graphite. It is often obtained in fluidized-bed deposition, possibly due to continuous surface regeneration by the mechanical rubbing action of the bed. An isotropic structure, observed by transmission electron microscopy, is shown in Fig. 7.4.^[11]

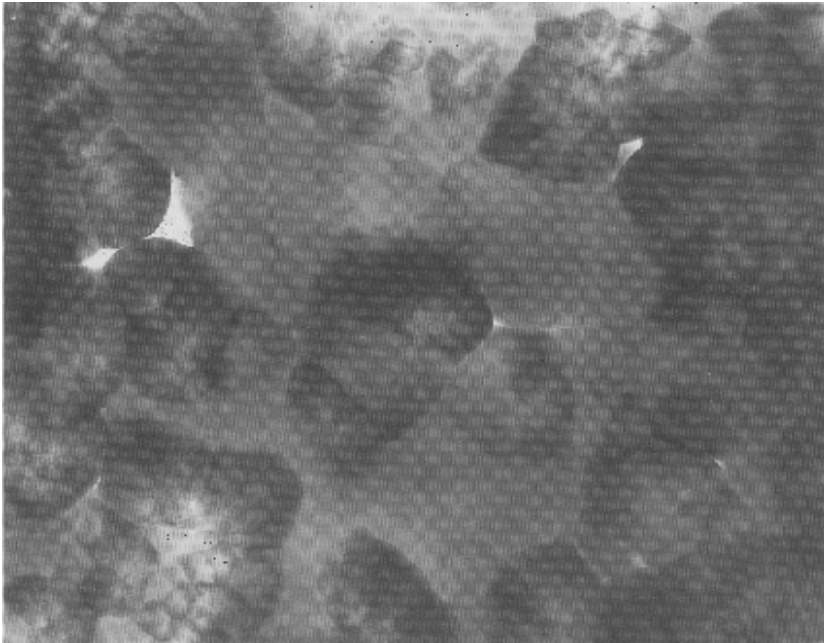


Figure 7.4. Structure of high-density ($\approx 2.0 \text{ g/cm}^3$) isotropic pyrolytic carbon, observed by transmission electron microscopy. Viewing plane is parallel to deposition plane ($x = 23\ 600$). (Photograph Courtesy J. L. Kaae, General Atomics, San Diego, CA)

2.6 Effects of Deposition Parameters

Effect of Pressure. CVD graphite with greater uniformity, better coverage, and improved quality is generally obtained at low deposition pressure. Pressure controls the thickness of the surface

boundary layer and consequently the degree of diffusion. At low pressure, the diffusion process is minimized and surface kinetics becomes the rate-controlling factor. Deposits obtained at low pressure tend to be isotropic.

At higher pressure (i.e., atmospheric), the reactant gas must be diluted with a non-reactive gas, such as hydrogen or argon, to prevent vapor-phase precipitation, while generally no dilution is necessary at low pressure. However, atmospheric-pressure reactors are usually simpler and cheaper, and, with proper control of the deposition parameters, satisfactory deposits may be obtained.

Effect of C/H Ratio. The carbon-to-hydrogen (C/H) ratio of the gas mixture (CH_4 and H_2) entering the reaction chamber is an important factor in the control of the nature of the deposition. Higher C/H ratios (such as 1/4) favor laminar deposition and lower ratios (such as 1/14) favor isotropic deposition.

Effect of Temperature. Generally, isotropic deposits are obtained at higher temperatures ($>1400^\circ\text{C}$) and laminar and columnar deposits at lower temperatures.

In summary, isotropic deposits are obtained at high temperature, low pressures, and low C/H ratio. The opposite conditions favor the deposition of laminar and columnar deposits.

2.7 Plasma-CVD of Graphite

The deposition of graphite is also obtained by plasma CVD, with the following deposition parameters:^[12]

- Gases: propylene-argon or methane-argon.
- Plasma: radio frequency (RF) at 0.5 MHz.
- Pressure: $<1300\text{Pa}$.
- Temperature: $300\text{--}500^\circ\text{C}$.

In a plasma-activated reaction, the substrate temperature can be considerably lower than in thermal CVD (see Ch. 5, Sec. 9). This allows the coating of thermally sensitive materials. The

characteristics and properties of the coating are similar to those of coatings deposited at higher temperatures ($>1000^{\circ}\text{C}$) (see Ch. 5).

2.8 Fluidized-Bed CVD of Graphite

The deposition of pyrolytic graphite in a fluidized bed is used in the production of biomedical components such as heart valves,^[13] and in the coating of uranium- and thorium-carbides nuclear-fuel particles for high temperature gas-cooled reactors, for the purpose of containing the products of nuclear fission.^[14] The carbon is obtained from the decomposition of propane (C_3H_8) or propylene (C_3H_6) at 1350°C , or of methane (CH_4) at 1800°C . Its structure is usually isotropic (see Ch. 4).

2.9 Applications of CVD Graphite

- Boats and crucibles for liquid phase epitaxy.
- Crucibles for molecular beam epitaxy.
- Electrodes for plasma etching.
- Reaction vessels for gas-phase epitaxy of III–V compounds.
- Trays for silicon-wafer handling.
- Heating elements for high temperature furnaces.
- Coating for fusion reactors.
- Coating for nuclear-fuel particles.
- Chemical vapor infiltration of carbon-carbon structures (reentry heat shields, rocket nozzles, and other aerospace components).^[15]
- Aircraft disk brakes.
- Biomedical devices, heart valves, implants.

3.0 THE CVD OF DIAMOND

3.1 The Structure of Diamond

The hybridization of the carbon atom from the ground state to the hybrid sp^3 (or tetragonal) orbital state accounts for the tetrahedral symmetry and the valence state of four with four $2sp^3$ orbitals found in the diamond atomic structure. These orbitals are bonded to the orbitals of four other carbon atoms with a strong covalent bond (i.e., the atoms share a pair of electrons) to form a regular tetrahedron with equal angles to each other of $109^\circ 28'$.^[1] Unlike graphite, the structure of diamond is isotropic. Each diamond tetrahedron combines with four other tetrahedra to form a strongly bonded, three-dimensional and entirely covalent crystalline structure, with a small bond length (0.154 nm) and a high bond energy (711 kJ/mol or 170 kcal/mol). Three representations of the structure are shown in Fig. 7.5.^{[16][17]}

3.2 Characteristics and Properties of Diamond

The compact structure of diamond accounts for its outstanding properties. It is the hardest of all materials with the highest thermal conductivity. It is the most perfectly transparent material and has one of the highest electrical resistivities and, when suitably doped, is an outstanding semiconductor material. The properties of CVD and single-crystal diamonds are summarized in Table 7.2.^{[1][18]–[20]}

Diamond is obtained as a polycrystalline material by CVD with properties similar to these of natural diamond. Efforts to produce single crystal thin films have so far been largely unsuccessful.

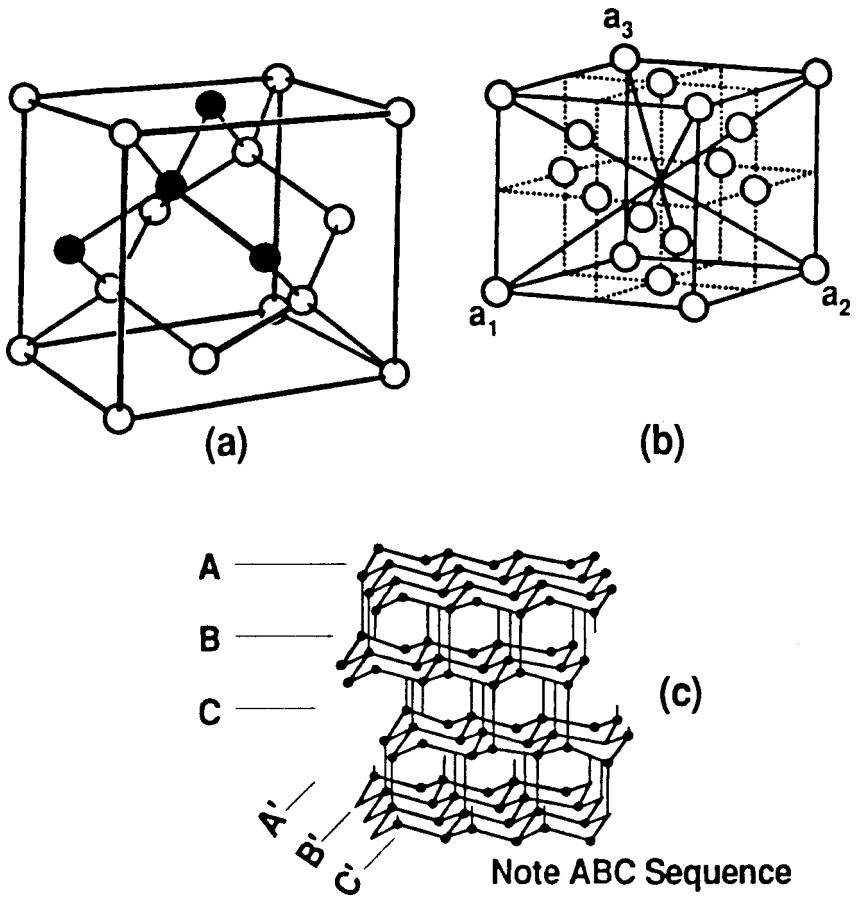


Figure 7.5. Structure of diamond.

3.3 Deposition Mechanism of CVD Diamond

A basic reaction in the CVD of diamond is based on the decomposition of a hydrocarbon, such as methane, as follows:

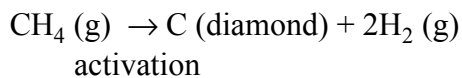


Table 7.2
Properties of Single-Crystal and CVD Diamond

	CVD Diamond	Single-Crystal Diamond
Density, g/cm ³	3.51	3.515
Specific heat, C_p , J/mol (at 300K)	6.195	6.195
Thermal conductivity at 25°C, W/m•K	2100	2200
Thermal expansion ($10^{-6}/^{\circ}\text{C}$ @ 25–200°C)	2.0	1.5–4.8
Index of refraction at 10μm	2.34–2.42	2.40
Bandgap, eV	5.45	5.45
Electrical resistivity, ohm•cm	10^{12} – 10^{16}	10^{16}
Dielectric constant (45 MHz–20 GHz)	5.6	5.70
Dielectric strength, V/cm	10^6	10^6
Loss tangent (45 MHz–20 GHz)	<0.0001	
Saturated electron velocity	2.7	2.7
Carrier mobilities (cm ² /V•s)		
electron (n)	1350–1500	2200
positive hole (p)	480	1600
Young's modulus, GPa	910–1250	1250
Compression strength, GPa	8.68–16.53	16
Vickers hardness range,* GPa	50–100	57–100
Coefficient of friction	0.05–0.15	0.05–0.15

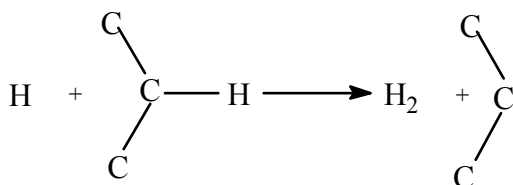
*Varies with crystal orientation

The deposition is a complex mechanism which is not fully understood at this time. Two conditions seem necessary: (a) activation of the carbon species and (b) the action of atomic hydrogen. These factors are reviewed in the following sections.

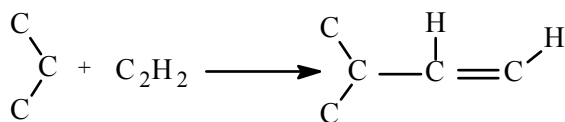
Deposition Precursors. Diamond has been deposited from a large variety of precursors which include, besides methane, aliphatic and aromatic hydrocarbons, alcohols, ketones, and solid polymers such as polyethylene, polypropylene, and polystyrene, and halogens.

These compounds generally decompose into two stable primary species: the methyl radical (CH_3) and acetylene (C_2H_2).^[21] The methyl radical is considered the dominant compound in generating the growth of CVD diamond.^{[22][23]} Direct deposition from acetylene, although difficult experimentally, has been accomplished, with a marked increase in the crystallinity of the diamond deposit.^[24]

Deposition Model. A two-step deposition model may be summarized as follows.^[25] In the first step, the diamond surface is activated by the removal of a surface-bonded hydrogen ion by atomic hydrogen as follows:



In the second step, the activated surface-carbon radical reacts with the carbon-hydrogen species (acetylene as a monomer unit) in the gas phase to become the site for carbon addition:



The model is consistent with experimental observations and should provide a useful guideline for future experiments. A similar model has been proposed that is based on the addition of a methyl group to one of the carbons followed by atomic hydrogen abstraction from the methyl group.^[26]

Role of Atomic Hydrogen. The stable hydrogen diatomic molecule (H_2) dissociates at high temperature ($>2000^\circ\text{C}$) or in a high current-density arc to form atomic hydrogen. The dissociation reaction is highly endothermic ($\Delta H = 434.1 \text{ KJmol}^{-1}$).

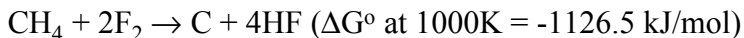
The rate of dissociation increases rapidly above 2000°C . It also increases with decreasing pressure.^[24] The rate of recombination (i.e., the formation of the molecule) is rapid since the mean-free-path dependent half-life of atomic hydrogen is only 0.3 sec.

Atomic hydrogen plays an essential role in the surface and plasma chemistry of diamond deposition as it contributes to the stabilization of the sp^3 dangling bonds found on the diamond surface plane. Without this stabilizing effect, these bonds would not be maintained and the diamond $\{111\}$ plane would collapse (flatten out) to the graphite structure.

The other function of atomic hydrogen is to remove graphite selectively. Unlike molecular hydrogen, atomic hydrogen is extremely reactive. It etches graphite twenty times as fast as it etches diamond and, when graphite and diamond are deposited simultaneously, graphite is preferentially removed while most of the diamond remains.^[27] These two effects of atomic hydrogen, graphite removal, and sp^3 bond stabilization, are believed essential to the growth of CVD diamond.

Effect of Oxygen and Oxygen Compounds. The presence of oxygen or an oxygen compound such as H_2O , CO , methanol, ethanol, or acetone, appears to be important contributor to diamond film formation. A small amount of oxygen added to methane and hydrogen tends to suppress the deposition of graphite by reducing the acetylene concentration as well as increasing the diamond growth rate.^{[21][28]} Adding water to hydrogen may increase the formation of atomic hydrogen, which would explain the observed increased deposition rate.

Halogen-Based Deposition. Diamond growth also occurs in several halogen-based reactions such as:



These reactions proceed at lower temperature (250–750°C) than those based on the methyl-radical mechanism reviewed above. The halogen reaction mechanism is still controversial and the optimum precursor species are yet to be determined.^[29] To proceed, the reactions must be highly favored thermodynamically. This is achieved when the reaction products are solid carbon and stable gaseous fluorides or chlorides (HF, HCl, SF₆).

The deposition is carried out in a simple flow tube. The amount of carbon-containing gas is maintained at <5% of the overall gas composition to retard formation of non-diamond carbon. The addition of oxygen or oxygen compounds (air, H₂O, CO₂) enhances growth.

3.4 CVD Processes for Diamond: Plasma Deposition

To deposit diamond by CVD, the carbon species must be activated since, at low pressure, graphite is thermodynamically stable and without activation only graphite would be formed. Activation is obtained by two energy-intensive methods: high temperature and plasma. CVD processes based on these two methods are continuously expanded and improved and new ones are regularly proposed.

Most CVD-diamond processes require a plasma (see Ch. 5, Sec. 9). Two types of plasma are currently used for the deposition of diamond: microwave plasma (non-isothermal) and arc plasma (isothermal).

Microwave-Plasma Deposition. The operating microwave frequency is 2.45 GHz. A typical microwave plasma for diamond deposition has an electron density of approximately 10²⁰ electrons/m³, and sufficient energy to dissociate hydrogen. A microwave-deposition reactor is shown schematically in Fig. 5.18 of Ch. 5.^{[28][30]}

The substrate (typically a silicon wafer) is positioned at the lower end of the plasma. Gases are introduced at the top of the reactor, flow

around and react at the substrate, and the gaseous by-products are removed through the exhaust. The substrate must be heated to 800–1000°C for diamond to form. This can be done by the interaction with the plasma and microwave power but this is difficult to regulate and, more commonly, the substrate is heated directly by radiant or resistance heaters which provide more accurate temperature control.

Typical microwave deposition conditions are the following:

Incident Power	600 W
Substrate Temp:	800–1000°C
Gas mixture H ₂ /CH ₄ :	50/1 to 200/1
Pressure:	10 to 5000 Pa
Total gas flow:	20–200 scm ³ /min

The morphology and properties of the deposited coating vary as a function of substrate temperature, gas ratio, and the intensity of the plasma at the deposition surface. Deposition rate is low, averaging 1–3 µm/h. This may be due to the limited amount of atomic hydrogen available in the deposition zone (estimated at 5%). An advantage of microwave plasma is its stability, which allows uninterrupted deposition lasting for days if necessary. However the plasma can be easily disturbed by the addition of oxygen-containing compounds.

Electron Cyclotron Resonance (ECR). A microwave plasma can also be produced by electron cyclotron resonance (ECR) (see Ch. 5, Sec. 9). An ECR-plasma reactor suitable for the deposition of diamond is shown schematically in Fig. 5.19 of Ch. 5.^[30]

An ECR plasma has two basic advantages for the deposition of diamond: (a) it minimizes the potential substrate damage caused by high-intensity ion bombardment, usually found in an standard high-frequency plasma where the ion energy may reach 100 eV, (b) it minimizes the risk of damaging heat-sensitive substrates since it operates at a relatively low temperature. Disadvantages are a more difficult process control and more costly equipment due to the added complication of the magnetic field.

Plasma-Arc Deposition. A plasma-arc is a high-intensity, low-frequency arc, generated between two electrodes by either direct or alternating current which requires a large amount of power and costly equipment.^[39]

Plasma-arc diamond deposition is produced at a higher pressure than in a microwave plasma (0.15 to 1 atm). At such pressure, the average distance traveled by the species between collisions (mean free path) is reduced and, as a result, molecules and ions collide more frequently and heat more readily.

By increasing the electrical energy in a fixed amount of gas, the temperature is raised and may reach 5000°C or higher.^[33] Such high temperatures produce an almost complete dissociation of the hydrogen molecules, the CH radicals, and other active carbon species. From this standpoint, arc-plasma deposition has an advantage over microwave-plasma or thermal CVD since these produce much less atomic hydrogen.

DC Plasma-Arc Equipment. A typical direct-current (DC) plasma-arc equipment is shown schematically in Fig. 7.6.^{[34][35]} Electrodes usually consist of a water-cooled copper anode and a tungsten cathode. Several gas-jet nozzles can be operated simultaneously and many design variations are possible, including separate input nozzles for hydrogen and methane (the latter mixed with argon) and the feeding of these gases in a coaxial feed electrode. Another design incorporates the interaction of a solenoid magnetic field to give the arc a helical shape. This stabilizes and increases the length of the arc.^[36]

The plasma jet can be cooled rapidly just prior to coming in contact with the substrate by using a blast of cold inert gas fed into an annular fixture. Gaseous boron or phosphorus compounds can be introduced into the gas feed for the deposition of doped-semiconductor diamond.^[37]

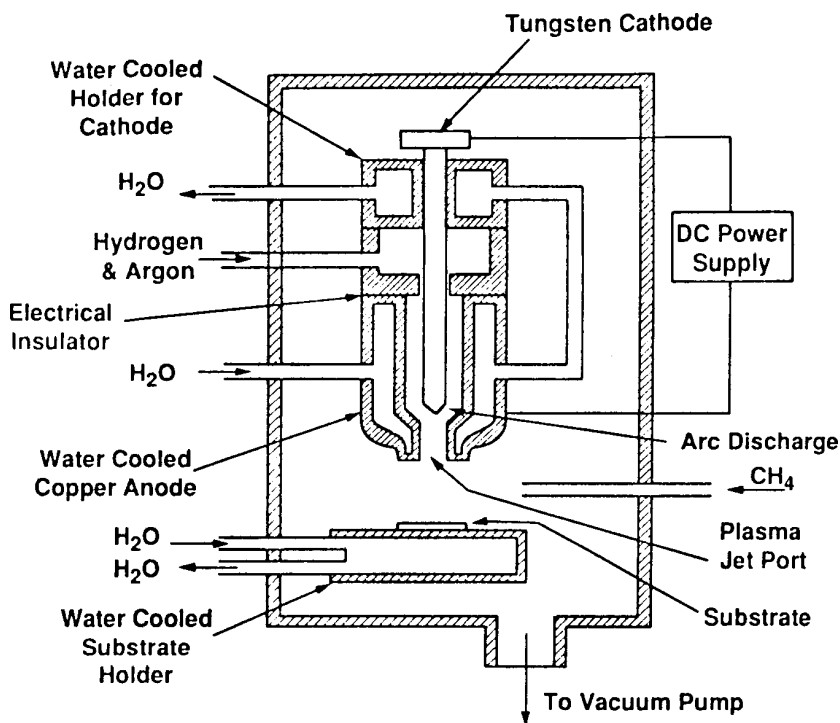


Figure 7.6. Schematic of arc-discharge apparatus for the deposition of diamond.

The sudden expansion of the gases, as they are heated in the arc plasma, causes the formation of a high-speed arc jet so that the atomic hydrogen and the reactive carbon species are transported almost instantly to the deposition surface and the chances of hydrogen recombination and of vapor-phase reactions are minimized.

The substrate may be heated to unacceptable levels by the high temperature of the gases and cooling is usually necessary. Temperature control and substrate cooling remain a problem in arc-plasma systems. However, deposition is rapid and efficient, high

rates of deposition (80 $\mu\text{m/h}$ or higher) are possible, and thick deposits are routinely produced.^[38] The availability of free-standing shapes, 15 cm in diameter and 1 mm thick, has recently been announced.^{[18][19]}

3.5 Thermal CVD (Hot Filament)

A plasma can be generated by high temperature which, in the case of diamond deposition, is obtained by a resistance-heated wire or tube made of tungsten or tantalum heated to 2000°C or slightly higher.^{[29][39]} A schematic of the equipment is shown in Fig. 7.7. Atomic hydrogen is formed and the carbon species become activated in the vicinity of the hot metal. The deposition rate and the composition and morphology of the deposit are functions of the temperature and the distance between the hot metal and the substrate. This distance is usually 1 cm or less. Much beyond that, most of the atomic hydrogen recombines and no diamond is formed.

The substrate temperature should be kept between 800 and 1000°C and cooling may be necessary. Gas composition and other deposition parameters are similar to those used in a microwave-plasma system. Deposition rate is low, reported as 0.5 to 1 $\mu\text{m/h}$.

A disadvantage of the hot-filament process is the short life of the metallic heater, which tends to carburize and embrittle rapidly. In this respect, tantalum performs better than tungsten with an estimated life of 600 hrs (vs. 100 hrs for tungsten).^[33] The heated metal may also evaporate and contaminate the diamond film. Furthermore, it is not advisable to add oxygen or an oxygen compound, as mentioned in Sec. 2.4, since, at these temperatures, tungsten (or most other refractory metals) would oxidize rapidly. However, the equipment is relatively inexpensive and experiments are readily carried out. Other heating-element materials, such as graphite or rhenium, are being investigated.^[40]

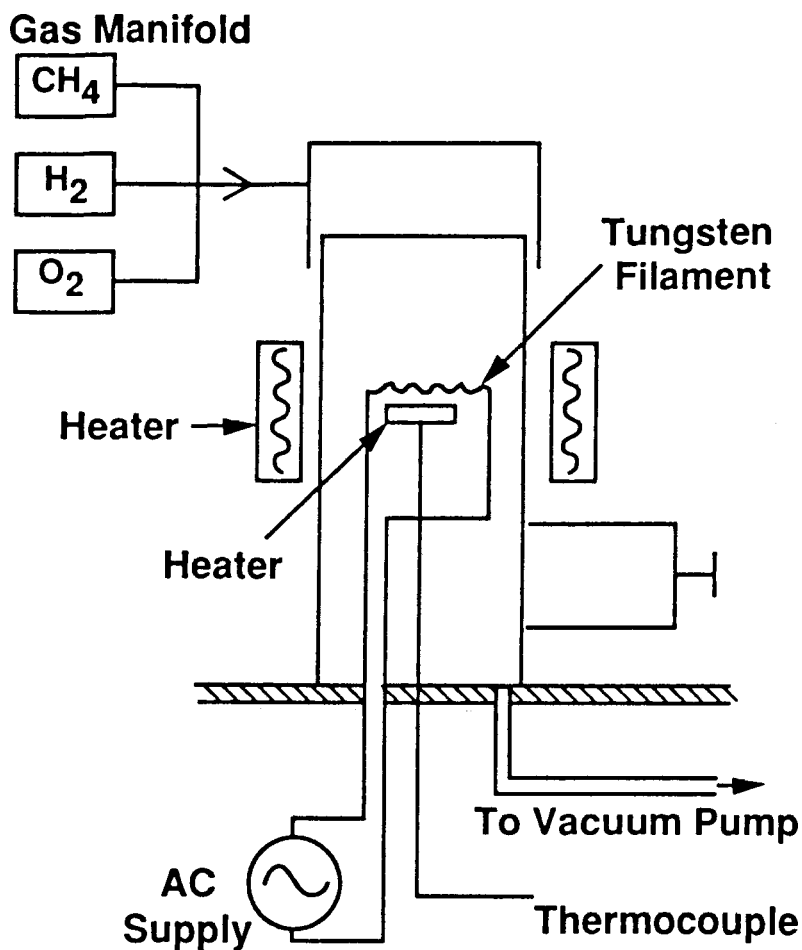


Figure 7.7. Schematic of hot-filament apparatus for the deposition of diamond.

3.6 Applications of CVD Diamond

Some actual and potential applications of CVD diamond are summarized in Table 7.3.^{[18][19]}

Table 7.3
Actual and Potential Applications of CVD Diamond

Grinding, cutting:	Inserts Twist drills Whetstones Industrial knives Circuit-board drills	Oil-drilling tools Slitter blades Surgical scalpels Saws
Wear parts:	Bearings Jet-nozzle coatings Slurry valves Extrusion dies Abrasive pump seals Computer disk coatings	Engine parts Medical implants Ball bearings Drawing dies Textile machinery
Acoustical:	Speaker diaphragms	
Diffusion, corrosion:	Crucibles Ion barriers (sodium)	Fiber coatings Reaction vessels
Optical coatings:	Laser protection Fiber optics Scanners Lenses	Antireflection UV to IR windows X-ray windows Radomes
Photonic devices:	Radiation detectors	Switches
Thermal management:	Heat-sink diodes Heat-sink PC boards	Thermal printers Target heat-sinks
Semiconductor:	High-power transistors High-power microwave Photovoltaic elements	Field-effect transistors UV sensors

4.0 THE CVD OF DIAMOND-LIKE-CARBON (DLC)

A new form of carbon coating is now available which is neither diamond nor graphite and is known as diamond-like carbon (DLC).^[1] DLC can be considered as a metastable carbon produced as a thin coating with a broad range of structure and composition.^{[41][42]}

DLC has properties similar to CVD diamond and it is easier to process without the high-temperature substrate requirements and with little restriction on size. However, it has several disadvantages: low deposition rate, high internal stress, and availability only in thin coatings. A number of important applications have been developed with a promising future.

4.1 Structure of DLC

DLC can be divided into two closely related categories known as amorphous DLC (a-C) and hydrogenated DLC (a-C:H). Amorphous DLC has less than one atomic % of hydrogen and is generally produced by sputtering from a solid carbon target. Hydrogenated DLC contains a variable and appreciable amount of hydrogen (up to 50 atomic %) and should be regarded as a hydrocarbon. It is the only form produced by CVD (a-C DLC is produced by sputtering) and is the only one considered here.

The structure of a-C:H DLC consists of an essentially amorphous network with isolated clusters dominated by the sp^2 configuration (graphite) with some sp^3 (diamond). Hydrogen is believed to play an essential role in determining the bonding configuration by helping to form the sp^3 bond, probably in a manner similar to the formation of CVD diamond.^[43]

4.2 Graphite, Diamond, and DLC

The differences between graphite, diamond, and DLC are summarized in Table 7.4.

Table 7.4
Comparison of Graphite, Diamond, and DLC

	Graphite	Diamond	DLC
Composition	Pure carbon carbon (<1 atm % hydrogen)	Essentially	Up to 50 atm % hydrogen
Microstructure	Crystalline	Crystalline	Amorphous
Atom-bonding state	sp ² only	sp ³ only	sp ² , sp ³ , sp ¹ (variable ratio)
Stability	Stable	Stable	Metastable
Raman spectrum	Sharp peak at 1580cm	Sharp peak at 1332 cm	Broad humps at 1330 & 1550 cm
Electrical conductivity	Conductor (ab dir.)	Insulator	Insulator

4.3 Summary of the Properties of DLC

The structure and composition of DLC may vary considerably and, as a result, so do some of its properties. This is not necessarily a disadvantage since it is often possible to control and tailor these properties to fit specific applications (for instance, the index of refraction). Its properties are generally similar to those of diamond, such as high hardness and chemical inertness, but different in some key areas. As opposed to diamond, DLC has a variable index of refraction and variable electrical conductivity, both a function of hydrogen content.

The properties of DLC are summarized and compared with those of CVD diamond in Table 7.5.^{[44]–[47]}

Table 7.5
Properties of DLC and CVD Diamond Coatings

	CVD Diamond	DLC
Density, g/cm ³	3.40 ± 0.10	1.8–2.8
Thickness range, μm	1–1000	0.1–5
Internal stress	Tensile (moderate)	Compressive (high) 1.3–1.6 GPa
Thermal conductivity at 25°C, W/m•K	>1300	400–1000
Bandgap, eV	5.48	0.8–3
Index of refraction @ 10 μm	2.34–2.42	1.8–2.4
Electrical resistivity, Ω•cm	10 ¹² –10 ¹⁶	10 ⁵ –10 ¹⁵
Dielectric constant (45 MHz–20 GHz)	5.6	8–12
Vickers hardness, Kg/mm ²	5000–10000	2000–9000
Coefficient of friction*	0.05–0.15	0.01–0.3
* Varies with humidity		

4.4 The CVD of DLC

Like diamond, DLC can be obtained by CVD by plasma action in a hydrocarbon atmosphere. Its deposition process differs from that of diamond in as much as the activation is not so much chemical (i.e., the use of hydrogen atoms) but physical. This physical activation is usually obtained by colliding accelerated ions produced by a high-frequency discharge.

This discharge does not produce high temperature. Consequently the substrate remains relatively cool ($<300^{\circ}\text{C}$) and a wide variety of substrate materials can be used including plastics. This, of course, is a major advantage which the present processing of diamond films does not possess.

The deposition principle is relatively simple and a schematic diagram of the equipment is shown in Fig. 7.8.^[48] A high-frequency RF gas discharge (13.56 MHz) is generated in a mixture of hydrogen and a hydrocarbon, such as methane or n-butane (C_4H_{10}). The asymmetry of the electrodes and the large difference in mobilities between electrons and ions result in the spontaneous generation of a negative potential on the substrate which, as a result, is bombarded by the ionized gas species. The coating thus obtained can be a DLC material or a soft polymer-like graphite depending on the applied energy. The coating of a large number of substrates is possible as long as they can be electrically contacted. Deposition rate is slow (0.5 to 2 $\mu\text{m/hr}$).

A similar process uses a 30 cm. hollow cathode ion source with its optics masked to 10 cm. Argon is introduced to establish the discharge followed by methane in a 28/100 ratio of methane molecules to argon atoms. The energy level is 100 eV, the acceleration voltage 600 V, and the resulting deposition rate 0.5 to 0.6 $\mu\text{m/hour}$.^[49]

Good surface preparation is essential, as in all deposition processes, and this can be achieved by chemically cleaning the substrate followed by sputter cleaning with argon just prior to the actual deposition.

With present deposition technologies, it is difficult, if not impossible, to produce thick DLC films as they tend to delaminate and separate from the substrate when the thickness is greater than approximately 0.5 μm . This is the result of high internal compressive stresses, which appear to be related to the hydrogen content of the material.^[50]

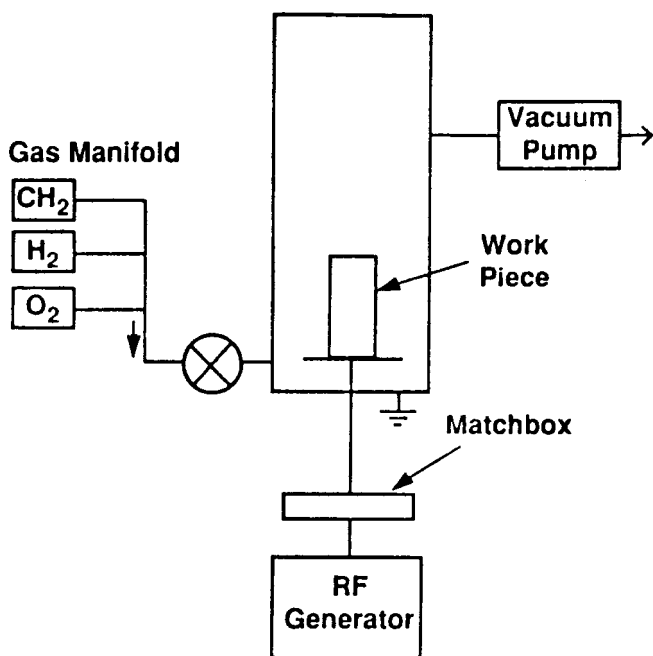


Figure 7.8. Schematic of apparatus for the deposition of a-C:H DLC.

4.5 Applications of DLC

DLC coatings are already in production in several areas (optical and IR windows) and appear particularly well-suited for abrasion and wear applications due to their high hardness and low coefficient of friction. They have an extremely smooth surface and can be deposited with little restriction of geometry and size (as opposed to CVD diamond). These are important advantages and DLC coatings will compete actively with existing hard coatings, such as titanium carbide, titanium nitride, and other thin film

materials. The major drawback of DLC is its lack of high temperature resistance, which may preclude it from cutting- and grinding-tool applications, and limitations in thickness to a few microns due to intrinsic stresses. DLC coatings are found in the following applications (see also Chs. 13 to 18 on applications of CVD):

- Erosion/corrosion protection for machinery and bearing surfaces.^[51]
- Anti-reflection (AR) coating with an adjustable index of refraction for germanium and zinc sulfide infrared windows.
- Abrasion and corrosion protection for germanium, magnesium fluoride, cadmium telluride, zinc sulfide, and zinc selenide IR windows.
- Laser-damage coatings for high-power laser windows.^[41]
- Etching mask for x-ray lithography.^{[42][50]}
- Coatings for hip joints, heart valves, and other prostheses. DLC is biocompatible and blood compatible.^[52]
- Coating for tissue culture flasks, microcarriers, cell culture containers, etc.

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8

The CVD of Non-Metallic Elements

1.0 INTRODUCTION

This chapter is a review of the CVD of non-metallic elements and covers boron, silicon, and germanium. Silicon and germanium are borderline elements with metalloid characteristics. Both are important semiconductor materials, particularly silicon, which forms the backbone of the largest business in the world: the electronic industry. All three materials are deposited by CVD on an industrial scale and a wide variety of CVD reactions are available.

2.0 THE CVD OF BORON

Boron is a light element produced by CVD in the form of coatings and fibers with limited industrial usage.

2.1 Properties of Boron

The properties of boron are summarized in Table 8.1.^[1]

Table 8.1
Properties of Boron at 25°C

Crystalline form: cubic (similar to diamond)

Lattice parameters: $a_0 = 5.4307 \text{ nm}$

Melting point, °C: 2050

Density, g/cm³: 2.35

Thermal conductivity, W/m·K: 60

Thermal expansion 0–100°C, ($\times 10^{-6}/^\circ\text{C}$): 4.8

Specific heat (J/mole·K): 11.16

(J/g·K): 1.032

Electrical resistivity, $\mu\Omega\text{cm}$: 1.8×10^{12}

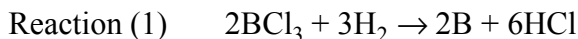
Young's modulus of elasticity, GPa: up to 480

Vicker hardness, GPa: 25.3

Boron has an hexagonal structure based on the icosahedron. It is an electrical insulator. It has good chemical resistance and is hard and brittle. Boron has excellent nuclear properties including a high neutron-absorption cross section (760 barn at neutron velocity of 2200 m/sec). The cross section of the B¹⁰ isotope is considerably higher (3840 barn).^[2] In addition, boron does not have decay products with a long half-life and high-energy secondary radioactive materials.

2.2 CVD Reactions

The hydrogen reduction of the chloride is the major production process^{[3][4]} with a deposition reaction is as follows:



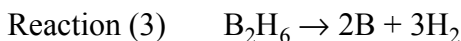
The deposition temperature range is 900–1300°C and the pressure is up to 1 atm. The kinetics of this reaction were studied by Tanaka.^[5] This reaction is used to produce boron fibers on an industrial scale (see Ch. 19).

The pyrolysis of the bromide has also been reported.^[6] The deposition reaction is as follows:



The deposition temperature range is 1000–1500°C and the pressure 1 Torr.

Boron is also obtained by the pyrolysis of diborane. Only moderate temperature is required (400–900°C) with a pressure up to 1 atm.^{[6][7]}



In addition to the thermal CVD reactions mentioned above, plasma CVD is used for the low temperature deposition of boron.^[8]

2.3 Applications

- Production of boron fibers on W or C core (see Ch.19).^[9]
- Coatings for the first wall of fusion reactor.^{[10][11]}
- Dopant in silicon semiconductor films.

3.0 THE CVD OF SILICON

3.1 Characteristics and Properties of Silicon

Silicon has the crystal structure of diamond and its properties are influenced by the crystal orientation.^[12] CVD silicon can be

either single crystal (epitaxial silicon), polycrystalline (polysilicon), or amorphous. The properties of the single crystal are summarized in Table 8.2.^[1]

Table 8.2
Properties of Silicon at 25°C

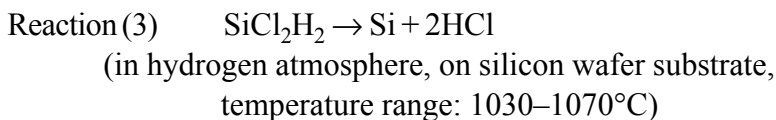
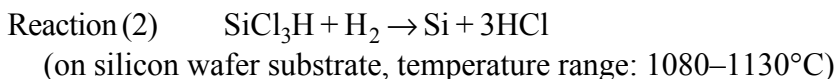
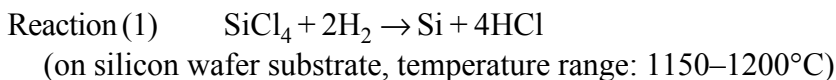
Crystalline form: cubic (similar to diamond)
Lattice parameters: $a_0 = 0.357$ nm
Melting point, °C: 1414
Density, g/cm ³ : 2.329
Thermal conductivity, W/m·K: 150
Thermal expansion 0–100°C, ($\times 10^{-6}/^\circ\text{C}$): 3
Specific heat (J/mole·K): 10.58
(J/g·K): 0.405
Electrical resistivity, $\mu\Omega\text{m}$: 3×10^8
Bandgap at 300K (eV): 1.12
Saturated Drift Velocity (cm/sec): 1.0×10^7
Drift Mobility.Electrons (cm/V·sec): 1500
Drift Mobility.Holes (cm/V·sec): 450
Breakdown Electric Field (V/cm): 3×10^5
Dielectric constant: 11.8
Maximum Junction Temperature (°C): ≈ 250

Semiconductor properties are imparted by doping its structure with boron, phosphorus, or arsenic atoms. Silicon is relatively inert chemically but is attacked by halogens and dilute alkalis. It has good optical transmission especially in the infra-red.

3.2 CVD Reactions

Several precursors and CVD reactions are available to deposit silicon. The deposit can be either single crystal (epitaxial), polycrystalline, or amorphous.

Silicon Epitaxy. Silicon epitaxial films have superior properties. The applications are, however, limited by the high temperature of deposition, which is generally above 1000°C. These reactions use chlorinated compounds of silicon (tetrachloride, trichlorosilane, or dichlorosilane) as precursors as follows:



Reactions (1), (2), and (3) are generally carried out at atmospheric pressure and produce films up to 100 μm thick. These reactions, which are used extensively in production, are reversible since the formation of HCl promotes the etching off of impurities during deposition due to the high energy states of silicon bonding at the sites of impurities.^{[13][14]}

As the density of devices placed on the silicon wafer increases, the problems of autodoping and interdiffusion become more acute and the high temperature limitation of the above reactions has prompted much experimental effort to develop epitaxial deposition at lower temperature. This has been accomplished in the following experimental developments:

- Deposition from silane (SiH_4) at low pressure (1 to 15 mTorr) at 750–800°C and by plasma deposition with a temperature range of 600–800°C.^{[14][15]}
- Deposition from disilane (Si_2H_6) in an RF induction heated reactor at 850°C.^[16]
- Deposition by rapid thermal heating with tungsten halogen lamp banks at 600–900°C.^{[17][18]}
- Deposition by CO_2 laser at 700°C.^[19]
- Plasma-enhanced deposition from silane (see below).
- Deposition from silane at ultrahigh vacuum.^[20]

Polycrystalline Silicon (Polysilicon). Polycrystalline silicon is used extensively in semiconductor devices. It is normally produced by the decomposition of silane at low pressure (ca. 1 Torr) as follows:



This reaction is irreversible. Epitaxial silicon is deposited. Polycrystalline silicon is obtained in the range of 610–630°C, which is close to the crystalline-amorphous transition temperature.^{[21][22]}

This reaction was also used to deposit epitaxial silicon at the temperature range of 1000–1040°C, but the deposit was generally unsatisfactory and the reaction is no longer used for that purpose. However, if the reaction is enhanced with a plasma using electron cyclotron resonance (ECR), fluxes may be independently controlled and high-quality epitaxial silicon deposits are obtained at temperatures below 500°C.^[23]

Amorphous Silicon. Amorphous silicon is generally deposited by Reaction (4) at a deposition temperature of 560°C and at low pressure (ca. 1 Torr).^[18] Helium RF plasma CVD is also commonly used, especially in the production of solar photovoltaic devices.^[24]

Electronic Grade Silicon (EGS). As the first step in the production of electronic grade silicon (EGS), an impure grade of silicon is pulverized and reacted with anhydrous hydrochloric acid, to yield primarily trichlorosilane, HSiCl_3 . This reaction is carried out in a fluidized bed at approximately 300°C in the presence of a catalyst. At the same time, the impurities in the starter impure silicon react to form their respective chlorides. These chlorides are liquid at room temperature with the exception of vanadium dichloride and iron dichloride, which are soluble in HSiCl_3 at the low concentration prevailing. Purification is accomplished by fractional distillation.

The next step is the hydrogen reduction of the trichlorosilane (Reaction 2 above). The end product is a polycrystalline silicon rod up to 200 mm in diameter and several meters in length. The resulting EGS material is extremely pure with less than 2 ppm of carbon and only a few ppb of boron and residual donors. The Czochralski pulling technique is used to prepare large single crystals of silicon, which are subsequently sliced into wafers for use in electronic devices.^[12]

3.3 Applications of CVD Silicon

Many applications of silicon are found in integrated circuits and other semiconductor devices and include the following (see Chs. 13–16 on applications of CVD).

Epitaxial Silicon

- Digital bipolar IC's.
- Linear digital metal-on-silicon (MOS).
- Discrete linear digital MOS.
- Complimentary MOS (CMOS).

Polysilicon

- Gate electrodes.
- Interconnection conductors.
- Resistor and emitter contacts.
- Thermal and mechanical sensors.
- Photovoltaic cells.

Amorphous silicon

- Photovoltaic devices.
- Photocopier drums.

Silicon is also alloyed with germanium ($\text{Si}_x\text{Ge}_{1-x}$) for applications such as heterojunction bipolar transistors and optical emitters (see next section).^{[25]–[27]}

4.0 THE CVD OF GERMANIUM

4.1 Characteristics and Properties

Germanium was the semiconductor material used in the development of the transistor in the early 1950s. However, it exhibits high junction leakage current due to its narrow bandgap and is now largely replaced by silicon. It is a brittle metalloid element with semiconductor characteristics. The properties of germanium are summarized in Table 8.3.^{[12][28]}

Table 8.3
Properties of Germanium at 25°C

Crystalline form: cubic (similar to diamond)

Lattice parameters: $a_0 = 0.56574$ nm

Melting point, °C: 936

Density, g/cm³: 5.323

Thermal conductivity, W/cm·K: 0.60

Thermal expansion 0–100°C, ($\times 10^{-6}/^\circ\text{C}$): 5.7

Specific heat (J/g·K): 0.31

Electrical resistivity, Ωcm : 4-40

Bandgap at 300K (eV): 0.66

Drift Mobility

Electrons (cm²/V·sec): 3800

Holes (cm²/V·sec): 1800

Hardness, Kg/mm²: 780

Flexural strength 13000psi

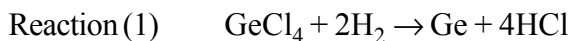
Young's modulus: 14.9 Mpsi

Poisson's ratio: 0.28

Max. operating temp (°C): 100 (150 for silicon)

4.2 CVD Reactions

Single crystal germanium can be deposited by the hydrogen reduction of the chloride at 600–900°C as follows:^[26]



It is now produced mostly from the decomposition of germane, usually at atmospheric pressure and at temperatures ranging from 600 to 900°C as follows:



Crystalline deposits are obtained with Reaction (2) in the temperature range of 350–400°C at low pressure (< 1 Torr).^[29] At still lower temperature (< 330°C) and moderate pressure (20–50 Torr), an amorphous germanium deposit is obtained.^[30] With Reaction (2), germanium is obtained by plasma CVD at 450°C and by laser CVD at 340°C.^{[31][32]}

Germanium is also deposited from metallo-organic precursors, such as tetrapropyl germanium, $\text{Ge}(\text{C}_3\text{H}_7)_4$ and tetraallyl germanium, $\text{Ge}(\text{C}_3\text{H}_5)_4$, with helium or hydrogen diluent. These reactions occur at low pressure and in the temperature range of 575–700°C.^[33]

4.3 Applications

A major use of germanium is as an alloy with silicon.^[34] A SiGe transistor with speed of over 60 GHz can allow as low as 1.5 V operation.^[35] Other reported applications are:

- Ge films on Si to tailor bandgap of heterostructures.^{[25][26]}
- Photovoltaic conversion.^[32]
- Photodetectors.

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9

The CVD of Ceramic Materials: Carbides

1.0 INTRODUCTION

The term ceramics originally referred to oxides only. This is no longer the case as the meaning has been considerably broadened and now includes, in addition to oxides, materials such as borides, carbides, nitrides, silicides, and the compounds of Group VIb, i.e., the chalcogenides (sulfides, selenides, and tellurides). The CVD of these ceramic materials is reviewed in this and the three following chapters. The number of ceramic materials is considerable and only those which have been the object of significant CVD investigations are considered in this book. The present chapter is a review of the carbides.

Carbides are hard and wear-resistant materials which have a high melting point, are thermally stable, and are generally chemically resistant (although their resistance to oxidation is generally poor). Their composition often varies over a wide range and, as a result, their properties may vary considerably. Some carbides, such as B_4C , SiC , TiC , and WC , are major industrial materials with numerous applications.^[1]

1.1 Refractory-Metal (Interstitial) Carbides

Carbides produced by CVD include the refractory-metal carbides and two important non-metallic carbides: boron carbide and silicon carbide. The refractory-metal carbides consist of those of the nine transition elements of Groups IVa, Va, and VIa and the 4th, 5th, and 6th Periods as shown below in Table 9.1.

Table 9.1
Refractory Metals in the Periodic Table

	Group IV	Group V	Group VI
4th Period	Titanium	Vanadium	Chromium
5th Period	Zirconium	Niobium	Molybdenum
6th Period	Hafnium	Tantalum	Tungsten

These carbides, also known as interstitial carbides, are crystalline compounds of a host metal and carbon. The host-metal atoms are generally arranged in a close-packed structure and the carbon occupies specific interstitial sites in that structure. Such a structure sets size restrictions on the two elements in order for the carbon atom to fit into the available sites and the population of these sites (if all are occupied) determines the stoichiometry of the carbide.

Structure. The structure of the refractory-metal carbides increases in complexity with increasing group number. Thus the carbides of Group IVa are characterized by a single cubic monocarbide. In those of Group Va, a M_2C phase exists as well as the monocarbide. The carbides of Group VIa are far more complex and have several compositions.

Oxygen and Hydrogen Contamination. A general problem in the CVD of refractory-metal carbides relates to potential oxygen contamination during deposition. Carbides can dissolve considerable quantities of oxygen by substitution for carbon. This is particularly true when the lattice is deficient in carbon.^[19] To avoid the deleterious effect of oxygen substitution, it is essential to maintain a deposition system that is completely free of oxygen. Likewise, hydrogen can dissolve readily in the carbon deficient carbides and, since many CVD reactions are carried out in hydrogen, this may easily occur. It may be necessary to vacuum anneal the coating to remove the hydrogen. Finally, composition uniformity can be a serious problem and the careful control of stoichiometry is necessary.

The interstitial carbides have the following general characteristics:

- They have a complex electronic bonding system which includes metallic, covalent, and ionic components.
- They are primarily non-stoichiometric phases.
- As ceramics, they have high hardness and strength.
- Like metals, they have high thermal and electrical conductivity.
- They allow non-metal vacancies (i.e., carbon) in the lattice.

1.2 Non-Metallic (Covalent) Carbides

The atomic and crystalline structure of the two non-metallic carbides, boron and silicon carbides, is less complex than that of the

interstitial carbides. These carbides are also known as covalent carbides, since their bonding is essentially covalent: the carbon atoms bond to the silicon or boron atoms by sharing a pair of electrons and, like all covalent bonds, these atoms form definite bond angles. The bonding is achieved by the hybridization of the valence electrons of the respective atoms.

The two covalent carbides have low density, low atomic weight, and useful semiconductor properties. They are extremely hard and strong materials which exhibit typical ceramic characteristics.

In this chapter, each carbide is listed alphabetically with its basic properties, its major CVD reactions and processes, and its present and potential applications.

2.0 THE CVD OF BORON CARBIDE

2.1 Characteristics and Properties

Boron carbide is a non-metallic covalent material with the theoretical stoichiometric formula, B_4C . Stoichiometry, however, is rarely achieved and the compound is usually boron rich. It has a rhombohedral structure with a low density and a high melting point. It is extremely hard and has excellent nuclear properties. Its characteristics are summarized in Table 9.2.

Chemical Resistance. Boron carbide resists oxidation in air up to 600°C due to the formation of a film of B_2O_3 . Its chemical resistance is generally excellent although it reacts with halogens at a high temperature.

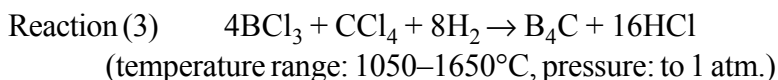
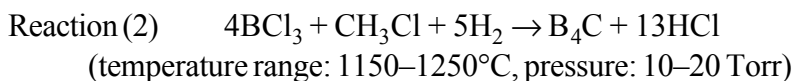
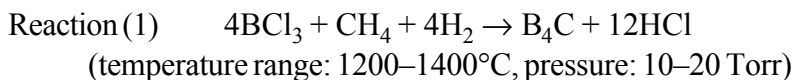
Table 9.2
Summary of Characteristics and Properties of Boron Carbide

Composition: (B ₁₁ C)CBC
Molecular Weight (g/mol): 55.26
Color: black (pure crystal is transparent and colorless)
X-ray Density (g/cm ³): 2.52
Melting Point: ≈2400°C (does not decompose)
Specific Heat (J/mole•K): 50.88
Heat of Formation (-ΔH) (kJ/mol.K at 298.15K): 57.8 ± 11.3
Thermal Conductivity (W/m•°C): 30
Thermal Expansion (10 ⁻⁶ /°C): 4.3
Electrical Resistivity (μΩcm): 0.1–10
Seebeck Coefficient (μV/K): 200–300 @ 1250
Vickers Hardness (GPa): 27.4–34.3
Modulus of Elasticity (GPa): 290–450
Shear Modulus (GPa): 165–200
Bulk Modulus (GPa): 190–250
Poisson's Ratio: 0.18
Flexural Strength (MPa): 323–430
Compressive Strength (MPa): 2750
Absorption Cross Section for Thermal Neutrons (barn): 755

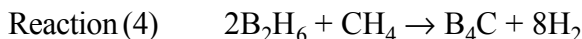
Note: Test temperature is 20°C unless otherwise stated

2.2 CVD Reactions

The following CVD reactions are commonly used to deposit boron carbide.^{[2]–[5]} All three reactions use excess hydrogen. The most common is Reaction (1).



Boron carbide has also been deposited from diborane as a boron source in a plasma at 400°C as follows:



2.3 Applications^{[6]–[9]}

- Coating for shielding against neutron radiation.
- Coating for neutron flux control in nuclear reactors.
- Wear parts, sandblast nozzles, seals.^[10]
- Mortar and pestle.
- High-grade abrasive and lapping powder.
- High-temperature thermocouple.
- Lightweight body and airborne armor.
- Matrix material for ceramic composites.
- Coating for nozzles, dressing sticks for grinding wheels.
- Matrix material for ceramic composites.^[11]

3.0 THE CVD OF CHROMIUM CARBIDE

3.1 Characteristics and Properties

Chromium carbide has three phases: Cr_{23}C_6 , Cr_7C_3 , Cr_3C_2 (major). The latter phase is the one reviewed here. Chromium carbide is an important material because of its excellent resistance to corrosion. It is the most oxidation resistant of all metal carbides. Its characteristics and properties are summarized in Table 9.3.

Chemical Resistance. The chemical resistance of chromium carbide is superior to that of other interstitial carbides. Oxidation in air starts at 1000°C and a dense and strong oxide layer is formed. It is insoluble in cold HCl but dissolves in hot oxidizing acids.

3.2 CVD Reactions

A common deposition reaction combines the metal chloride with a hydrocarbon, such as butane, at an optimum deposition temperature of 1000°C .^[12] Other hydrocarbons can also be used. Another useful reaction is the decomposition of the chromium dicumene $\text{Cr}[(\text{C}_6\text{H}_5)\text{C}_3\text{H}_7]_2$ in a temperature range of $300\text{--}550^\circ\text{C}$ and at pressures of $0.5\text{--}50$ Torr.^[13]

3.3 Applications

- Special coating for maximum chemical resistance.
- Intermediate layer for tool steel coatings.

Table 9.3
Characteristics and Properties of Chromium Carbide (Cr_3C_2)

Crystal Structure and Lattice Parameters (nm): Orthorhombic, $a = 0.283$, $b = 0.554$, $c = 1.1470$ Cr_3C_2 is an intermediate carbide having carbon chains with C-C distance approximately 0.165 nm running through distorted metal lattice where the Cr atoms are at the corners of trigonal prisms and the carbon atoms in the center of the prisms. ^{[1][4]} Space Group and Pearson Symbol: Pnma, oP20 Composition: narrow range of homogeneity (approx- imately 39–40 at/°C) Molecular Weight: 180.01 g/mol Color: gray X-ray Density: 6.74 g/cm ³ Melting Point: 1810°C (decomposes at melting temperature)
Specific Heat (C_p): 32.7 J/mole•K Heat of Formation ($-\Delta aH_f$) at 298K (KJ/g-atom metal) (1): 23.0 Thermal Conductivity: 19 W/m•°C at 20°C Thermal Expansion: $10.4 \times 10^{-6}/^\circ\text{C}$ at 20°C
Electrical Resistivity: 75 $\mu\Omega\text{cm}$ Superconductive Transition Temperature: <1.2K Hall Constant: $-0.47 \times 10^{-4} \text{ cm}^3/\text{A}\cdot\text{s}$
Vickers Hardness: 10–18 GPa Young Modulus of Elasticity: 15.5–24.5 GPa Transverse Rupture Strength: 49 MPa

Note: Test temperature is 20°C unless otherwise stated

4.0 THE CVD OF HAFNIUM CARBIDE

4.1 Characteristics and Properties

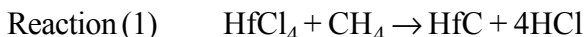
Hafnium carbide (HfC) is an interstitial carbide which, with tantalum carbide, is the most refractory compound known. Its characteristics and properties are summarized in Table 9.4.

Chemical Resistance. Hafnium carbide oxidizes in air at 500°C. It is not as chemically resistant as TiC and is similar to ZrC in that respect.

Isomorphism. Like TiC and ZrC, HfC forms solid solutions with oxygen and nitrogen, which have a wide range of composition. HfC forms solid solutions with the other monocarbides of Group IV and V, particularly NbC.^[14]

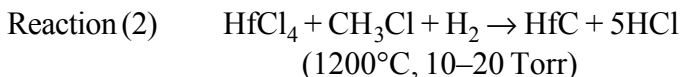
4.2 CVD Reactions

HfC is produced by CVD mostly on an experimental basis. The most common deposition system is the reaction of the metal chloride with a hydrocarbon, which can be propane (C₃H₈), propene (C₃H₆), toluene (C₇H₈), or methane (CH₄) as follows:^{[15]–[17]}



The chloride is usually generated *in situ*. This reaction occurs over a wide range of temperature (900–1500°C) and pressure from 10 Torr to atmospheric. Whisker formation has been observed at 1 atm and 1230°C.

Another deposition reaction is as follows:



Usually carbides with a composition approaching stoichiometry are obtained at the lower deposition pressure and carbon-deficient carbides at higher pressure.

Table 9.4
Characteristics and Properties of Hafnium Carbide

Structure: cubic close packed (f.c.c. B1, NaCl)
Lattice Parameter: 0.4636 nm
Space Group: <i>Fm3m</i>
Pearson Symbol: cF8
Composition: $\text{HfC}_{0.60}$ to $\text{HfC}_{0.99}$. Composition rarely reaches stoichiometry and HfC is normally metal rich.
Molecular Weight: 190.50 g/mol
Color: silver gray
X-ray Density : 12.67 g/cm ³
Melting Point: 3928°C (melts without decomposition)
Debye Temperature: 436K
Specific Heat(C_p): 37.4 J/mole•K
Heat of Formation, $-\Delta H$, at 298K (kJ/g-atom metal) (5): 209.6
Entropy at 298.15K (S°): 39.48 KJ/mol
Thermal Conductivity: 20.0(W/m•°C)
Thermal Expansion: 6.6 (x 10 ⁻⁶ /°C)
Electrical Resistivity: 37–45 $\mu\Omega\text{cm}$
Superconductive Transition Temperature: < 1.2K
Hall Constant: - 12.4 x 10 ⁻⁴ cm•A•s
Magnetic Susceptibility: -23 x 10 ⁻⁶ emu/mol
Vickers Hardness: 26.1 GPa
Modulus of Elasticity: 350–510 GPa
Shear Modulus: 193 GPa
Bulk Modulus: 241 GPa
Poisson's Ratio: 0.18

Note: Test temperature is 20°C unless otherwise stated

4.3 Applications

In spite of its excellent properties, hafnium carbide has only limited industrial importance, possibly because of its high cost. Some experimental applications are as follows:

- Oxidation resistant coatings for carbon-carbon composites (co-deposited with SiC).^[18]
- Production of whiskers (with nickel catalyst).
- Coating for superalloys.
- Coating on cemented carbides.
- HfC-NbC solution as coating for tools.^[14]

5.0 THE CVD OF NIOBIUM CARBIDE

5.1 Characteristics and Properties

Niobium carbide, also known as columbium carbide, is a important refractory material with a high melting point. It is used as a CVD coating mostly on an experimental basis. Niobium carbide has two phases: Nb₂C and the monocarbide NbC. The latter is the only phase of industrial importance and the only one reviewed here. Its characteristics and properties are summarized in Table 9.5.

Chemical Resistance. NbC oxidizes in air at 800°C. It reacts with nitrogen and ammonia at a high temperature to form NbN. It is less chemically resistant than TaC. It is dissolved by hot oxidizing acids.

Isomorphism. NbC, NbN, and NbO have isotypical structures and form solid solutions where nitrogen or oxygen can substitute for carbon over a wide range of homogeneity. These solutions may be considered as Nb(C,N,O) mixed crystals. NbC forms solid solutions with the carbides of Group IV and the other monocarbides of Group V, and with the nitrides of Group IV and V.^[14]

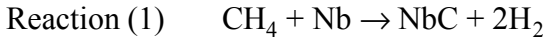
Table 9.5
Characteristics and Properties of Niobium Carbide

Structure and Lattice Parameter (nm) ccp, $a = 0.44691$
Space Group and Pearson Symbol Fm $\bar{3}$ m, cF8
Composition: NbC _{0.70} to NbC _{0.99}
Molecular Weight: 104.92 g/mol
Color: gray sometimes with a lavender tint
X-ray Density: 7.85 g/cm ³
Melting Point: 3600°C (melts without decomposition)
Debye Temperature: 546K
Specific Heat (C_p): 36.8 J/mole•K
Heat of Formation ($-\Delta H_f$) at 298K (kJ/g-atom metal): 140.6
Thermal Conductivity: 14.2(W/m•°C)
Thermal Expansion: $6.6 \times 10^{-6}/^\circ\text{C}$
Electrical Resistivity: 35 $\mu\Omega\text{cm}$
Superconductive Transition Temperature: 6K
Hall Constant: $-1.3 \times 10^{-4}\text{cm}^3/\text{A}\cdot\text{s}$
Magnetic Susceptibility: $+15.3 \times 10^{-6}\text{emu/mol}$
Vickers Hardness: 19.65 GPa
Modulus of Elasticity: 338–580 GPa
Shear Modulus: 214 GPa
Bulk Modulus: 296 GPa
Poisson's Ratio: 0.21
Transverse Rupture Strength: 300–400 MPa

Note: Test temperature is 20°C unless otherwise stated

5.2 CVD Reactions

Niobium carbide may be obtained by carburization of the metal substrate according to the following reaction at low pressure and at temperatures above 2000°C:



It can also be produced by the hydrogen reduction of the respective chlorides at 1500–1900°C, over a wide range of pressures:[19]



5.3 Applications

NbC has only limited industrial uses. It is found mostly in combination with TaC in 10, 20, or 50 wt% NbC. The following is a summary of its applications in production or development.

- In special grades of cemented carbides in combination with alumina.
- With TaC to improve the properties of cemented carbides.
- Hard coating for the protection of niobium metal.
- As a carbonitride for superconductor applications.[20][21]

6.0 THE CVD OF SILICON CARBIDE

6.1 Characteristics and Properties

Silicon carbide (SiC) is a major industrial material with a considerable number of applications. CVD plays a significant role in its development and production.[1] SiC is a covalent carbide with two phases: α and β . The phase of major interest here is β SiC, which has a cubic zinc blend structure. It is the one reported here.

Beta SiC (β SiC) has good chemical resistance, particularly to oxidation owing to the formation of a thin adherent and protective film of silicon dioxide on the surface. Its characteristics are summarized in Table 9.6.

Table 9.6
Summary of Characteristics and Properties of β -Silicon Carbide

Composition: SiC (narrow range)	
Molecular Weight (g/mol): 40.097	
Color: colorless to yellow if pure, brown if doped with boron, nitrogen or aluminum	
X-ray Density (g/cm ³): 3.214	
Melting Point: 2545°C at 1 atm.; 2830°C at 35 atm. (decomposes to Si, SiC, Si ₂ , and SiC ₃)	
Specific Heat (J/mol•K): 28.63	
Heat of Formation (- ΔH) (kJ/mol.K at 298.15K): - 28.03 \pm 2	
Thermal Conductivity (W/m•°C): 25.5	
Thermal Expansion (x 10 ⁻⁶ /°C): 3.8	
Dielectric Constant @ 300K: 9.72	
Electrical Resistivity ($\mu\Omega\text{cm}$): 10 ⁻² to 10 ⁶	
Debye Temperature: 1430K	
Energy Gap (eV): 2.6	
Exiton Energy Gap (eV) @ 4.2K: 2.39	
Superconductive Transition Temperature: 5K	
Refractive Index, n, (Na) 2.48:	
2.7104 @ 467 μm	2.6916 @ 498 μm
2.6823 @ 515 μm	2.6600 @ 568 μm
2.6525 @ 589 μm	2.6446 @ 616 μm
2.6264 @ 691 μm	
Vickers Hardness (GPa): 24.5 – 28.2 (varies with crystal face)	
Modulus of Elasticity (GPa): 475 @ 293K	
441 @ 1773K	
Shear Modulus (GPa): 192	
Bulk Modulus (GPa): 96.6	
Elastic Constants (dynes/cm ²): C11 2.89, C12 2.34, C44 0.544	
Poisson Ratio: 0.142	
Flexural Strength (MPa): 350–600	

Note: Test temperature is 20°C unless otherwise stated

Chemical Resistance. The oxidation resistance of SiC is excellent due to the formation of a layer of SiO₂ on the surface. It is inert to most chemicals at room temperature.

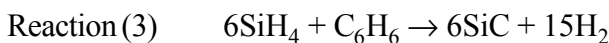
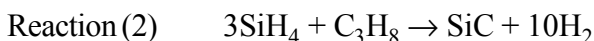
6.2 CVD Reactions

Most SiC deposition systems involve the Si-C-H-Cl chemical combination. A very commonly used reaction is the decomposition of methyl trichlorosilane (MTS):^{[22]–[24]}



This reaction is carried out in a temperature range of 900–1400°C (optimum 1100°C) and at total pressures of 10–50 Torr in a hydrogen atmosphere. The deposition rate and the crystallite size increase with increasing partial pressure of MTS. Other precursor combinations are: SiCl₄/CH₄, SiCl₄/CCl₄, SiH₂Cl₂/C₃H₈, and SiHCl₃/C₃H₈.^[25] The decomposition of MTS is also used in connection with gravity driven SiC, see particles added to the gas phase. Increase in deposition rate is claimed.^[26]

Another common deposition system is based on the reaction of silane with a hydrocarbon such as propane or benzene in the following simplified reactions:^{[22][28]}



The useful temperature range is lower than that of Reaction (1) with 800°C being typical. A pressure of approximately 10 Torr is typical, although atmospheric pressure can also be used.^[28] Plasma CVD has been used with Reactions (2) and (3) to deposit SiC at considerably lower temperatures (200–500°C).^[29]

The decomposition of methyl silane (CH_3SiH_3) is used to produce an amorphous SiC at 800°C and a crystalline SiC at 900°C .^[30] A two-step growth procedure produces SiC films from hexamethyldisilane and 8% H_2/Ar mixture at ambient pressure and low temperature.^[31]

A composite film of SiC and diamond was produced from tetramethylsilane, hydrogen, and methane in a microwave plasma on single-crystal silicon wafers. Volume fraction of the components can be adjusted by varying the gas composition.^[32]

A SiC buffer layer was grown on a silicon wafer at $1150\text{--}1300^\circ\text{C}$ from one to 45 minutes using C_3H_8 and H_2 as reactant gases. The thickness of the film increased gradually by diffusion of Si into the deposit until a thickness controlled by temperature and silicon etching was reached.^[33]

6.3 Applications

The CVD technology of SiC has resulted in many industrial applications summarized below.^[34]

- Low-weight, high-strength mirrors.
- High-power, high-frequency, and high-temperature semiconductor devices.^[35]
- Radiation-resistant semiconductors.
- Radiation sensors (amorphous SiC).
- Fibers and whiskers (see Ch.19).
- Matrix in ceramic composites.
- Catalytic support for automobile exhaust.
- Thermocouple sheath.
- Lightweight armor.
- Coatings for susceptors and heating elements for

epitaxial silicon deposition.^[36]

- Coatings for fusion reactor applications.^[37]
- Coatings for ceramic heat exchanger tubes.
- Oxidation resistant coatings for carbon-carbon composites.
- Heteroepitaxial deposit on silicon.
- Blue light-emitting diodes (LED).
- Fibers and whiskers.

7.0 THE CVD OF TANTALUM CARBIDE

7.1 Characteristics and Properties

Tantalum carbide (TaC) is a refractory interstitial carbide with a high melting point. It is structurally and chemically similar to niobium carbide. It has two phases: Ta₄C and the monocarbide TaC. The latter is the only phase of industrial importance and the only one described here. The characteristics and properties of TaC are summarized in Table 9.7.

Chemical Resistance. TaC oxidizes rapidly in air at 800°C. Otherwise it is one of the most chemically stable carbides. It decarburizes when heated in hydrogen at very high temperatures (3000°C). It does not react with nitrogen up to 2700°C. It reacts at high temperature with Nb, Ta, and Mo. It is stable in nonoxidizing acids, but is attacked easily by HNO₃ and HF and by melts of oxidizing salts.

Isomorphism. TaC forms solid solutions with the carbides of Group IV and the other monocarbides of Group V and with the mononitrides of these two groups.^[14]

Table 9.7
Characteristics and Properties of Tantalum Carbide

Structure, Lattice Parameter (nm): ccp, $a = 0.4455$
Space Group and Pearson Symbol: Fm3m, 3F8
Composition: TaC _{0.73} to TaC _{0.99}
Molecular Weight: 192.96 g/mol
Color: brown, gold
X-ray Density : 14.5 g/cm ³
Melting Point: 3950°C (melts without decomposing)
Debye Temperature: 489K
Specific Heat (C_p): 36.4 J/mole•K
Heat of Formation ($-\Delta H_f$) at 298K (kJ/g-atom metal): 142.7
Thermal Conductivity: 22.1 W/m•°C at 20°C
Thermal Expansion: $6.3 \times 10^{-6}/^{\circ}\text{C}$ at 20°C
Electrical Resistivity: 25 $\mu\Omega\text{cm}$
Superconductive Transition Temperature: 10.3K
Hall Constant: $-1.1 \times 10^{-4} \text{ cm}^3/\text{A}\cdot\text{s}$
Magnetic Susceptibility: $+9.3 \times 10^{-6} \text{ emu/mol}$
Vickers Hardness: 16.7 GPa
Modulus of Elasticity: 285–560 GPa
Shear Modulus: 214 GPa
Bulk Modulus: 414 GPa
Poisson's Ratio: 0.24
Transverse Rupture Strength: 350–400 MPa

Note: Test temperature is 20°C unless otherwise stated

7.2 CVD Reactions

TaC can be obtained by the carburization of a tantalum substrate or coating at low pressure and at temperatures above 2000°C:[38]



It can also be produced by the hydrogen reduction of the respective chlorides at 1150–1200°C and a pressure of 10–20 Torr:



The metal chloride is usually produced *in situ* at 550–600°C (see Ch. 4, Sec. 3.1)

7.3 Applications

The CVD of TaC has few industrial applications. It has been used as a coating on tantalum metal to improve chemical resistance, high-temperature hardness, and wear and oxidation resistance.

8.0 THE CVD OF TITANIUM CARBIDE

8.1 Characteristics and Properties

Titanium (TiC) is an important industrial material produced extensively by CVD. It is an excellent refractory material which is unusually hard with high strength and rigidity and outstanding wear resistance. Its properties are summarized in Table 9.8.

Table 9.8
Summary of Characteristics and Properties of Titanium Carbide

Structure: cubic close packed (f.c.c. B1, NaCl) (25)
Lattice Parameter: 0.4328 nm
Space Group: <i>Fm3m</i>
Pearson Symbol: cF8
Composition: $\text{TiC}_{0.47}$ to $\text{TiC}_{0.99}$
Molecular Weight: 59.91 g/mol
Color: silver gray
X-ray Density : 4.91 g/cm ³
Melting Point: 3067°C (does not decompose)
Debye Temperature: 614K
Specific Heat (C_p): 33.8 J/mole•K
Heat of Formation, $-\Delta H$, at 298K (kJ/g-atom metal) (5): 184.6
Thermal Conductivity (K): 21 W/m•°C
Thermal Expansion: $7.4 \times 10^{-6}/^\circ\text{C}$
Electrical Resistivity: $50 \pm 10 \mu\Omega\text{cm}$
Superconductive Transition Temperature: 1.15K
Hall Constant: $-15.0 \times 10^{-4} \text{ cm}^3\text{A}^{-1}\text{s}^{-1}$
Magnetic Susceptibility: $+6.7 \times 10^{-6} \text{ emu/mol}$
Vickers Hardness: 28–35 GPa
Modulus of Elasticity: 410–510 GPa
Shear Modulus: 186 GPa
Bulk Modulus: 240–390 GPa
Poisson's Ratio: 0.191
Transverse Rupture Strength: 240–390 MPa
Coefficient of Friction: 0.25 (on tool steel, 50% humidity)

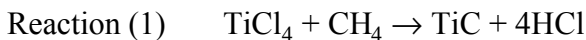
Note: Test temperature is 20°C unless otherwise stated

Chemical Resistance. TiC oxidizes slowly in air at 800°C. It is resistant to most acids. It is attacked by HNO₃, HF, and the halogens. It can be heated in hydrogen to its melting point without decomposition.

Isomorphism. TiC is isomorphous with TiN and TiO. Thus oxygen and nitrogen as impurities, or as deliberate addition, can substitute for carbon to form binary and ternary solid solutions over a wide range of homogeneity. These solutions may be considered as Ti(C,N,O) mixed crystals. TiC forms solid solutions with the other monocarbides of Group IV and V. It is the host lattice for WC.^[14]

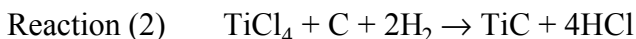
8.2 CVD Reactions

The most common deposition system is the reaction of the metal chloride with a hydrocarbon as follows:



This reaction is usually carried out at a temperature range of 850–1050°C in a hydrogen atmosphere and at pressure varying from less than 1 Torr to 1 atm. Above 1300°C, single crystal TiC is deposited.^{[38]–[40]} Other carbon sources, such as toluene and propane, have also been used.^[39] Reaction (1) is also used in a plasma at a lower temperature range (700–900°C) and lower pressure (1 Torr).^[42]

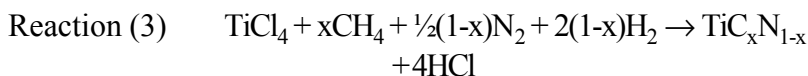
TiC is also produced by reacting the chloride with a carbon substrate in excess hydrogen, in the temperature range of 1750–1800°C. The reaction is as follows:



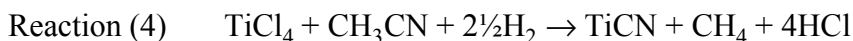
Recent investigations with MOCVD have shown that TiC can be deposited at lower temperature (ca. 700°C).^[43] Metallorganics that are used include the following:

- Tris-(2,2'-bipyridine) titanium (decomposes at 370–520°C).
- Tetraneopentyl titanium (decomposes at 150–300°C).
- Dichlorotitacene, $(C_5H_5)_2TiCl_2$, (substrate temperature is 700°C).

Titanium Carbonitride. Titanium carbonitride (TiC_xN_{1-x}) combines the wear properties of TiC with the low friction and oxidation and chemical resistance of TiN. It is obtained in a hydrogen atmosphere and at a temperature of approximately 1000°C by the following simplified reaction:



If acetonitrile (CH_3CN) is used as a carbon and nitrogen source, the deposition temperature is greatly reduced and the process can be used to coat tool steel.^{[44][45]} The reaction is carried out at low pressure and at a temperature range of 700–900°C. It is as follows (in simplified form):



8.3 Applications

- Secondary carbide in cemented carbides.
- Coatings for cutting and milling tools and inserts.
- Coatings for stamping, chamfering, and coining tools.

- Ball-bearing coatings.^[46]
- Coatings for extrusion and spray gun nozzles.
- Coatings for pump shafts, packing sleeves, and feed screws for the chemical industry.
- Coatings for molding tools and kneading elements for plastic processing.
- Molded bipolar plates for high-voltage battery and fuel power sources.^[47]
- Coatings for fusion-reactor applications.^[48]

9.0 THE CVD OF TUNGSTEN CARBIDE

9.1 Characteristics and Properties

Tungsten carbide has a complex crystal structure with three phases: W_C (subcarbide), the monocarbide WC (also called α -WC), and β - WC_{1-x} , which is unstable and forms only above 1530°C. The monocarbide WC is the most important phase and the one reported here. Its characteristics and properties are summarized in Table 9.9.

Chemical Resistance. Oxidation in air starts at 500–600°C. WC is resistant to acids and is not attacked at room temperature by mixtures of HF and HNO_3 but is attacked by these acids at elevated temperature. It is attacked by chlorine above 400°C and by fluorine at room temperature. It is stable in dry hydrogen to melting point.

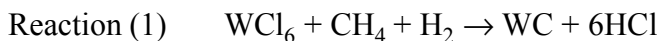
Table 9.9
Characteristics and Properties of Tungsten Carbide (WC)

Crystal Structure and Lattice Parameters (nm): hexagonal, a 0.2907, c 0.2837
Space Group and Pearson Symbol: P6m2, hP2
Composition: Narrow range of homogeneity, α -WC _{0.98} WC _{1.00}
Molecular Weight: 195.86 g/mol
Color: gray
X-ray Density: 15.8 g/cm ³
Melting Point: 2870°C (decomposes by melting incongruently)
WC has a large stability domain but reacts with W _C or W
Debye Temperature: 493K
Specific Heat (C _p): 39.8 J/mole•K
Heat of Formation (-ΔaH _f) at 298K (KJ/g-atom metal (1): 37.7
Thermal Conductivity: 63 W/m•°C
Thermal Expansion: a 5.2, c 7.3
Electrical Resistivity: 17–22 μΩcm
Superconductive Transition Temperature: 10.0K
Hall Constant: - 21.8 x 10 ⁻⁴ cm ³ /A•s at 20°C
Magnetic Susceptibility: + 10 x 10 ⁻⁶ emu/mol
Vickers Hardness: 22 GPa (as opposed to other carbides, the hardness is maintained at high temperature with little change. It is still 18 GPa at 800°C).
Young's Modulus of Elasticity: 620–720 GPa
Shear Modulus: 262 GPa
Poisson's Ratio: 0.18
Transverse Rupture Strength: 550 MPa

Note: Test temperature is 20°C unless otherwise stated

9.2 CVD Reactions

Most CVD reactions use the halides as a source of metal as follows:^{[49][50]}

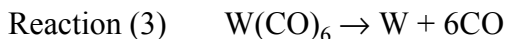


The temperature range for Reaction (1) is 670–720°C. Deposition is usually done at a pressure of a few Torr and in excess hydrogen.

Another reaction uses methanol as a carbon source over a wide range of pressure from a few Torr to 1 atm:



Tungsten carbonyl is also used as a metal source at 350–400°C but carbon tends to remain incorporated in the structure.^[38] The reaction is as follows:



9.3 Applications

Tungsten carbide is a major industrial material used extensively in cemented carbides for cutting tools. Its main CVD applications are as follows:

- Production of submicron powder for hot pressing or hot isostatic pressing of high-precision tooling (see Ch. 19).
- Coating of fine-porosity carbon for catalytic applications.^[51]

10.0 THE CVD OF ZIRCONIUM CARBIDE

10.1 Characteristics and Properties

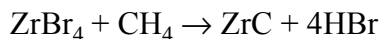
Zirconium carbide (ZrC) is a refractory interstitial carbide with a high melting point. It is produced by CVD mostly on an experimental basis although it has some nuclear applications. Like TiC, cubic ZrC has a variable composition and forms solid solutions with oxygen and nitrogen over a wide range of composition. Its characteristics and properties are summarized in Table 9.10.

Chemical Resistance. ZrC oxidizes in air at 800°C. It is not as chemically resistant as TiC and is similar to HfC in that respect. It is dissolved by cold HNO₃ and by a cold mixture of H₂SO₄ and H₃PO₄. It reacts readily with the halogens. It can be heated in hydrogen to its melting point without decomposition.

Isomorphism. Like TiC, ZrC forms solid solutions with oxygen and nitrogen, which have a wide range of composition. The lattices of ZrC, ZrN, and ZrO are isotypical. ZrC forms solid solutions with the other monocarbides of Group IV and V.^[14]

10.2 CVD Reactions

A common CVD reaction uses the bromide as a metal source at a temperature range of 1350–1550°C in an atmosphere of hydrogen and argon:^[52]



Zirconium carbide has also been deposited from the tetrachloride with methane or cyclopropane as the carbon source.^[53]

Table 9.10
Characteristics and Properties of Zirconium Carbide

Structure: cubic close packed (f.c.c. B1, NaCl)
Lattice Parameter: 0.4698 nm
Space Group: <i>Fm3m</i>
Pearson Symbol: cF8
Composition: $\text{ZrC}_{0.55}$ to $\text{ZrC}_{0.99}$
Molecular Weight: 104.91 g/mol
Color: silver gray
X-ray Density : 6.59 g/cm ³
Melting Point: 3420°C (melts without decomposition)
Debye Temperature: 491K
Specific Heat (C_p): 37.8 J/mole•K
Heat of Formation, $-\Delta H$, at 298K (kJ/g-atom metal) (5): 196
Thermal Conductivity: 20.5 W/m•°C
Thermal Expansion: $6.7 \times 10^{-6}/^\circ\text{C}$
Electrical Resistivity: $45 \pm 10 \mu\Omega\text{cm}$
Superconductive Transition Temperature: < 1.2K
Hall Constant: $-9.42 \times 10^{-4} \text{ cm}^3/\text{A}\cdot\text{s}$
Magnetic Susceptibility: $-23 \times 10^{-6} \text{ emu/mol}$
Vickers Hardness: 25.5 GPa
Modulus of Elasticity: 350–440 GPa
Shear Modulus: 172 GPa
Bulk Modulus: 207 GPa
Poisson's Ratio: 0.191

Note: Test temperature is 20°C unless otherwise stated

10.3 Applications

Zirconium carbide is a highly refractory compound with excellent properties but, unlike titanium carbide, it has found only limited industrial importance except as coating for atomic-fuel particles (thoria and urania) for nuclear-fission power plants.^[54] This lack of applications may be due to its high price and difficulty in obtaining it free of impurities.

11.0 THE CVD OF MISCELLANEOUS CARBIDES

Other carbides, besides those listed above, have been produced by CVD, mostly on an experimental basis. These materials are generally of lesser industrial interest at the present time and are listed here for reference purposes:

- Beryllium carbide, BeC , produced by the pyrolysis of metallo-organic compounds.^[38]
- Germanium carbide, GeC , produced by the reaction of acetylene and germane.^[55]
- Molybdenum carbide, MoC , produced by the decomposition of the carbonyl.^[56]
- Thorium carbide, ThC_2 , deposited from the iodide.^[38]
- Uranium carbide, UC_2 , deposited from the iodide.^[38]
- Vanadium carbide, VC , deposited from the chloride and methane.^[38]

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10

The CVD of Ceramic Materials: Nitrides

1.0 GENERAL CHARACTERISTICS OF NITRIDES

The nitrides reviewed here are those which are commonly produced by CVD. They are similar in many respects to the carbides reviewed in Ch. 9. They are hard and wear-resistant and have high melting points and good chemical resistance. They include several of the refractory-metal (interstitial) nitrides and three covalent nitrides: those of aluminum, boron, and silicon. Most are important industrial materials and have a number of major applications in cutting and grinding tools, wear surfaces, semiconductors, and others. Their development is proceeding at a rapid pace and CVD is a major factor in their growth.

1.1 Refractory-Metal (Interstitial) Nitrides

Interstitial nitrides are crystalline compounds of a host metal and nitrogen, where the nitrogen atom occupies specific interstitial

sites in the metal structure, which is generally close packed.^[1] The nine early-transition elements form interstitial nitrides (see Table 9.1 of Ch. 9). These materials are similar to interstitial carbides in structure and composition, and the two groups of materials closely resemble each other. The nitrides, however, are not quite as refractory, particularly those of Group VI, i.e., chromium, molybdenum, and tungsten nitrides; these compounds have poor thermal and chemical stability, and are not considered here.^[1]

The interstitial nitrides have several important characteristics in common with the interstitial carbides.

- They have a complex electronic bonding system, which includes metallic, covalent, and ionic components.
- They are primarily non-stoichiometric phases.
- They have high hardness and strength.
- Like metals, they have high thermal and electrical conductivity.
- Like the carbides, they allow nonmetal vacancies (i.e., nitrogen) in the lattice.
- Unlike the carbides, they tolerate metal-atom vacancies.

More so than the carbides, the interstitial nitrides are susceptible to the presence of even minute amounts of impurities such as hydrogen and particularly oxygen which tend to distort the structure. To avoid such harmful contamination, it is necessary to maintain a deposition system that is completely free of oxygen and hydrogen.

1.2 Covalent Nitrides

The atomic and crystalline structure of the three covalent nitrides, aluminum, boron, and silicon nitrides, is less complex than that of the interstitial nitrides. Their bonding is essentially covalent,

that is, the nitrogen atoms bond to the aluminum, boron, or silicon atoms by sharing pairs of electrons and, like all covalent bonds, these atoms form definite bond angles. The bonding is achieved by the hybridization of the valence electrons of the respective atoms.

The three covalent nitrides have the following common features and are in many ways similar to the covalent carbides reviewed in Ch. 9:

- They have high melting point and thermal and chemical stability.
- All three have similar cubic structures (although boron nitride also has a graphite-like structure).
- They have low density and low atomic weight.
- They are good electrical insulators.
- They are hard and strong materials and exhibit typical ceramic characteristics.
- All three are produced industrially by CVD with important applications.

In this chapter, each nitride is listed alphabetically with its basic properties, its major CVD reactions and processes, and its present and potential applications.

2.0 THE CVD OF ALUMINUM NITRIDE

2.1 Characteristics and Properties

Aluminum nitride is a highly stable covalent compound with the unusual combination of high thermal conductivity (comparable to that of metals) and high electrical insulation (comparable to the

best insulators). Its characteristics and properties are summarized in Table 10.1.^{[1]–[4]}

Table 10.1
Summary of Characteristics and Properties of Aluminum Nitride

Composition: AlN
Molecular Weight: 40.99 g/mol
Color: White when pure, tan or gray with impurities
X-ray Density: 3.16 g/cm ³
Space Group: F43m
Pearson Symbol: hP4
Direct band gap (2H polytype): 6.28 eV
Melting Point: 2200°C at 4 atm. N ₂ (sublimes at atm. pressure)
Specific Heat: 0.7–0.9 J/g.K, 28.7–36.9 J/mol.K
Thermal Conductivity (W/m•°C): up to 320 for single crystal
Thermal Expansion (10 ⁻⁶ /°C): 2.7 at 25°C (matches that of silicon)
Electrical Resistivity: 10 ¹³ Ω•cm
Direct Bandgap: 6.28 eV
Dielectric Constant: 8.9 at 1 MHz, 8.2 at 7 GHz
Dielectric Strength: 10 kV/mm
Surface Acoustic Velocity, Raleigh V ^R : 6–6.2 km/s, V _L = 11–12 km/s
Optical: transparent in the visible and near IR range. Piezoelectric characteristics
Vickers Hardness: 12 GPa
Young's Modulus: 315 GPa
Flexural Strength: 390–490 MPa
Poisson's Ratio: 0.25
Flexural Strength: 590–970 MPa
Compressive Strength: 2070 MPa

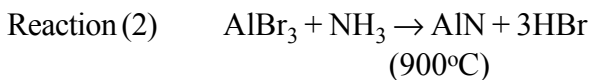
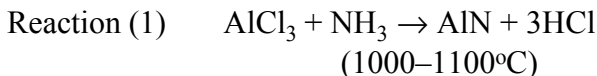
Note: Test temperature is 20°C unless otherwise stated

Chemical Resistance. AlN is resistant to oxidation up to 1350°C.^[21] It decomposes slowly in boiling water. It is essentially inert to most other chemicals at room temperature.

2.2 CVD Reactions

In many CVD reactions for the deposition of nitrides, ammonia (NH₃) is used as a source of nitrogen, rather than nitrogen. This is preferable from a thermodynamic standpoint but may present a problem in that any NH₃ — either unreacted or present in the regions of furnace where the temperature is below its dissociation temperature— tends to combine with the HCl effluent gas and forms NH₄Cl, which may clog the exhaust line.

AlN is produced by CVD in the form of coatings and powder both experimentally and on a production basis by the following high temperature reactions in a hydrogen atmosphere at low pressure (1 Torr) with ammonia and either the chloride or the bromide as metal sources:^[5]



Reaction (2) is also used with a plasma at a deposition temperature of 200–800°C.^[6] Reaction (1) in combination with TiCl₄ will produce a binary nitride, (Ti_{1-x}Al_x)N, also in a plasma at low temperature.^[7]

AlN is now often produced by MOCVD by reacting ammonia with trimethyl aluminum at low pressure (< 1 Torr), in the temperature range 900–1400°C.^{[8][9]}



The pyrolysis of aluminum-nitrogen organic complexes, such as diethyl aluminum azide $[(C_2H_5)_2AlN_3]$, is also used successfully at low deposition temperatures (450–870°C).^[10] Another metallo-organic, hexakis(dimethylamido)dialuminum, reacting with ammonia allows deposition at 200–250°C at atmospheric pressure.^[11]

2.3 Applications

The major application of CVD aluminum nitride is for electronic components. At this time, most of the AlN powder is produced by CVD and originates in Japan and is used by the Japanese industry.^[12]

- Heat-sink substrates and packaging materials for electronic devices (major application).
- Passivation and dielectric layers.
- High-frequency acoustic wave devices (piezoelectric).
- Traveling-wave tubes.
- Microwave-absorbing components.
- Experimental high-power and high-temperature material for electronic and optoelectronic devices especially in the UV region of the spectrum.

3.0 THE CVD OF HEXAGONAL BORON NITRIDE

3.1 Characteristics and Properties of h-BN

Boron nitride has two crystalline forms, hexagonal (h-BN) and cubic (c-BN), with much different properties. Hexagonal BN is the more important and has many industrial applications. Its structure is similar to that of graphite which it resembles in many ways. It has a very large anisotropy in the crystal with resulting anisotropic properties.

H-BN is produced by hot-pressing the powder or by CVD. The processes impart different properties. The hot-pressed material shows less anisotropy than the CVD BN, since the powder grains are randomly oriented. CVD BN is usually a turbostratic boron nitride with warped basal planes and lattice defects. It is also known as pyrolytic boron nitride or PBN.^{[13][14]}

Table 10.2
Summary of Characteristics and Properties
of CVD Hexagonal Boron Nitride

Composition: BN
Molecular Weight: 24.816 g/mol
Color: white to transparent
Density: 2.1 g/cm ³
Porosity (helium admittance): 2×10^{-11} cm.sec
Space Group: F43m
Thermal Conductivity (W/m•°C): ab 62.8; c 1.66 (at 100°C)
Thermal Expansion ($\times 10^{-6}/^{\circ}\text{C}$): ab 0; c 24 in the range of 20–250°C
Electrical Resistivity ($\Omega\cdot\text{cm}$): ab 10^7 , c 10^{15} (at 1000°C)
Loss Tangent (100 Hz to 1000 GHz): ab 1.5×10^{-4} ; c $< 1 \times 10^{-4}$
Dielectric Constant: ab 5.12; c 3.4
Hardness: soft and lubricious
Compressive Strength (MPa): c 234
Tensile Strength (MPa): ab 41; ab 103 (at 2200°C)
Torsional Shear Strength (Mpa): 10 (15 at 1500°C)
Young's Modulus (GPa): ab 22
Poisson Ratio: ab 0.25

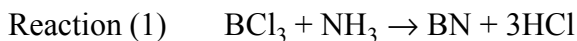
Notes: a) ab: tested in ab direction parallel to surface
c: tested in c direction (perpendicular to the surface)
b) Test temperature is 20°C unless otherwise stated

Like graphite, h-BN is soft and lubricious and it has a low density. It is a refractory material which sublimates at 3000°C and has exceptional chemical resistance. The characteristics and properties of CVD h-BN are shown in Table 10.2.

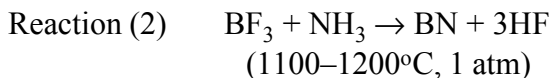
Chemical Resistance. Hexagonal boron nitride is one of the most outstanding corrosion-resistant materials. It is inert to gasoline, benzene, alcohol, acetone, chlorinated hydrocarbons, and other organic solvents. It is not wet by molten aluminum, copper, cadmium, iron, antimony, bismuth, silicon, germanium, nor by many molten salts and glasses. It has good resistance to oxidation and in this respect is far superior to graphite. It has no appreciable weight loss in air up to 1300°C. Above that, it oxidizes slowly by the formation of a protective layer of B₂O₃. It is essentially inert to all reagents at room temperature.

3.2 CVD Reactions

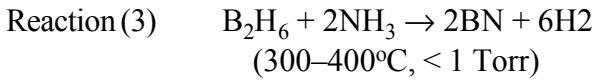
Coatings and monolithic components of h-BN are usually produced by CVD by the reaction of a boron halide with ammonia. MOCVD and plasma-CVD are also used. The reaction of boron trichloride and ammonia is as follows:^[15]



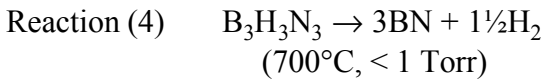
At a deposition temperature of 1300°C., a low-density material is obtained (1.5 g/cm³). Density increases with increasing temperature and reaches 2.0 g/cm³ at 1600°C. Vapor phase precipitation can be a problem in the high-temperature range. A more convenient reaction uses boron fluoride:



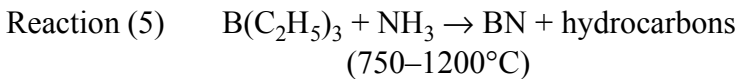
Low-temperature deposition is possible from diborane as a boron source:^{[16][17]}



Another useful deposition reaction is the decomposition of borazine. This is a condensation reaction which produces an amorphous BN with residual hydrogen incorporation:^[18]



MOCVD has also been used with triethyl boron as the boron source in a hydrogen and argon atmosphere:^[19]



3.3 Applications

The applications of hexagonal boron nitride form an important market, mostly as powder for lubricants and additives.^[28] Many of these applications are produced by CVD.

- Radar windows and antennas.
- Crucibles for aluminum evaporation and for molecular beam epitaxy.
- Vessels for Czochralski crystal growth of III–V and II–VI compounds (i.e., gallium arsenide).
- Insulating substrate in ribbon heaters in combination with a pyrolytic graphite resistance heating element.

4.0 THE CVD OF CUBIC BORON NITRIDE

4.1 Characteristics and Properties of c-BN

Cubic boron nitride (c-BN) is a different material altogether from h-BN, with a structure similar to that of diamond, which is characterized by extremely high hardness (second to diamond) and high thermal conductivity.^{[1][21]–[23]} As such, it is a material of great interest and a potential competitor to diamond, particularly for cutting and grinding applications. Its characteristics and properties are shown in Table 10.3

Table 10.3
Summary of Characteristics and Properties
of Cubic Boron Nitride

Composition: BN
Molecular Weight: 24.816 g/mol
Color: white
X-ray Density: 3.48 g/cm ³
Melting Point: 3000°C (sublimes)
Specific Heat: 12.65 J/mol•K
Thermal Conductivity: 300–600 W/m•°C (theoretical value: 1300)
Thermal Expansion: $4.9 \times 10^{-6}/^{\circ}\text{C}$
Electrical Resistivity: insulator
Hardness: 29.89–43.12 GPa (depending on crystal orientation)
Compressive Strength: 2730 MPa
Young's Modulus: 650 GPa
Fracture Toughness: 6.4 MPa•m ^{0.5}

Note: Test temperature is 20°C unless otherwise stated

Chemical Resistance. C-BN is essentially inert to all reagents at room temperature. It does not react with carbide formers such as Fe, Co, Ni, Al, Ta, and B at approximately 1000°C (while diamond does); this is a useful characteristic in machining and grinding applications. However, it reacts with aluminum at 1050°C and with Fe and Ni alloys containing Al above 1250°C.^[24]

4.2 CVD Reactions

Like synthetic diamond, C-BN is normally obtained by high-pressure processing. Efforts to synthesize it by CVD at low pressure are promising. It is deposited in an electron-cyclotron-resonance (ECR) plasma from a mixture of BF_3 and either ammonia or nitrogen at 675°C on an experimental basis.^[13] Like CVD diamond, it is also deposited by the hot-filament method using diborane and ammonia diluted with hydrogen at 800°C.^[25]

4.3 Other Boron Nitride Structures

Polycrystalline boron nitride films, with a structure similar to rhombohedral boron carbide and a ratio of boron to nitrogen of 3:1, were produced by hot-filament CVD. This work indicates the possible existence of other boron-nitride structures.^[26]

5.0 THE CVD OF HAFNIUM NITRIDE

5.1 Characteristics and Properties

Hafnium nitride (HfN) is a refractory which is resistant to chemical attack. It is produced by CVD mostly on an experimental basis. Its properties and characteristics are summarized in Table 10.4.

Table 10.4
Characteristics and Properties of Hafnium Nitride

Phase: HfN (major)
Structure: fcc B1 (NaCl),
Lattice Parameter: $a = 0.452 \text{ nm}$
Space Group: Fm3m
Pearson Symbol: cF8
Composition: $\text{HfN}_{0.75}$ to $\text{HfN}_{1.12}$
Molecular Weight: 192.497
Color: greenish yellow
X-ray Density : 13.8 g/cm^3
Melting Point: 3387°C
Debye Temperature: 421 K
Specific Heat (C_p): 38 J/mol.K
Heat of Formation ($-\Delta H_f$) at 298K: $369.4 \text{ kJ/g-atom metal}$
Thermal Conductivity (K): $21.7 \text{ W/m}\cdot^\circ\text{C}$
Thermal Expansion: $6.9 \times 10^{-6}/^\circ\text{C}$
Electrical Resistivity: $33 \mu\Omega\cdot\text{cm}$
Superconductive Transition Temperature: $2\text{--}8.7 \text{ K}$ (varies with composition)
Vickers Hardness: 16.3 GPa

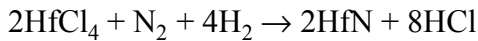
Note: Test temperature is 20°C unless otherwise stated

Chemical Resistance. HfN begins to oxidize in air at approximately 800°C. It is chemically stable at room temperature and is slowly attacked by concentrated acid solution with rising temperature.

Isomorphism. HfN is completely and mutually soluble with the nitrides and carbides of Groups IV and V with the exception of VN and VC (see Ch. 7).

5.2 CVD Reactions

The following reaction is used in excess hydrogen at a temperature range of 900–1300°C and at low pressure (ca. 10 Torr):^[27]



A similar reaction with ammonia as a nitrogen source at 1100°C has a much higher deposition rate owing to the high reactivity of the monatomic nitrogen released in the ammonia decomposition.

5.3 Applications

- Tribological and corrosion resistant coatings.
- Diffusion barriers for microelectronic devices (experimental).
- Whiskers.^[28]
- Coatings on tungsten wires.^[27]
- Coatings for cutting tools.

6.0 THE CVD OF NIOBIUM NITRIDE**6.1 Characteristics and Properties**

Niobium nitride (also known as columbium nitride) has three phases: Nb_2N , Nb_4N_3 , and NbN . The mononitride, NbN , is the most common phase and the only one reviewed here. NbN is an excellent superconductor. It is produced by CVD mostly on an experimental basis. Its characteristics and properties are summarized in Table 10.5.

Table 10.5
Characteristics and Properties of Niobium Mononitride

Structure & Lattice Parameters: hcp $a = 0.4395 \text{ nm}$,
 $c = 0.4338 \text{ nm}$

Space Group: $\text{P6}_3/\text{mmc}$

Pearson Symbol: hP8

Composition: $\text{NbN}_{0.92}$ to $\text{NbN}_{1.06}$

Molecular Weight: 106.91

Color: dark gray

X-ray Density: 7.3 g/cm^3

Melting Point: near 2400°C

Debye Temperature: 307 K

Specific Heat (C_p): $39.01 \text{ J/mol}\cdot\text{K}$

Heat of Formation ($-\Delta H_f$) at 298K: $236 \text{ kJ/g-atom metal}$

Thermal Conductivity (K): $3.76 \text{ W/m}\cdot^\circ\text{C}$

Thermal Expansion: $10.01 \times 10^{-6}/^\circ\text{C}$

Electrical Resistivity: $58 \mu\Omega\cdot\text{cm}$

Superconductive Transition Temperature: 16 K

Hall Constant: $-0.52 \times 10^{-4} \text{ cm}^3/\text{A}\cdot\text{s}$

Magnetic Susceptibility: $+31 \times 10^{-6} \text{ emu/mol}$

Vickers Hardness: 13.3 GPa

Modulus of Elasticity: 493 GPa

Note: Unless otherwise stated, test temperature is 20°C

Chemical Resistance. NbN begins to oxidize in air at approximately 800°C. It is chemically stable at room temperature. It is slowly attacked by concentrated acid solution with rising temperature.

Isomorphism. NbN is completely and mutually soluble with the nitrides and carbides of Groups IV and V (see Ch. 7).

6.2 CVD Reactions

The following reaction is used in excess hydrogen at a temperature range of 1000–1100°C and low pressure (ca. 10 Torr):



The reaction of the chloride with nitrogen has also been used.^{[29][30]} Lower deposition temperature is possible by MOCVD via the pyrolysis of a dialkylamide at 500–800°C.^[31]

6.3 Applications

- As a potential superconductor coating.^[29]
- Diffusion barrier in semiconductors (experimental).

7.0 THE CVD OF SILICON NITRIDE

7.1 Characteristics and Properties

Silicon nitride (Si_3N_4) is a major industrial material which is produced extensively by CVD for electronic and structural applications. It is an excellent electrical insulator and diffusion barrier (to sodium and water vapor) and has replaced CVD oxides in many semiconductor

devices. It is found as an amorphous material or in two hexagonal crystalline forms, α and β , the latter being the high-temperature form. An irreversible transformation from α to β occurs at 1600°C. The material has excellent overall properties such as:

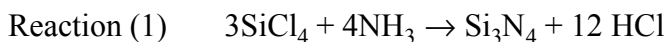
- Light weight.
- High strength and toughness (for a ceramic material).
- High chemical resistance to acids, bases, salts, and molten metals.
- Good resistance to oxidation to 1500°C.
- High electrical resistivity.

Its characteristics and properties are summarized in Table 10.6.^{[1][32][33]}

Chemical Resistance. Silicon nitride is resistant to oxidation up to 1350°C. It is resistant to most reagents at room temperature.

7.2 CVD Reactions

An important reaction for the deposition of silicon nitride combines silicon tetrachloride (SiCl_4) and ammonia:



The optimum deposition temperature is 850°C. Pressure may be up to 1 atm. A hydrogen or nitrogen atmosphere is used with very high ratio of N_2 to reactants (ca. 1000/1).^{[34]–[36]}

Another reaction uses dichlorosilane (SiH_2Cl_2), also with ammonia:

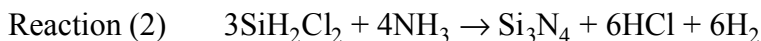


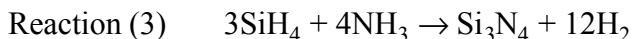
Table 10.6
Characteristics and Properties of Silicon Nitride

Composition: Si_3N_4
Molecular Weight: 140.28 g/mol
Color: colorless if pure
Theoretical Density (g/cm^3): 3.187 (β), 3.184 (α)
Melting Point: 1900°C
Specific Heat ($\text{J/g}\cdot\text{K}$): 0.54–0.7
($\text{J/mole}\cdot\text{K}$): 75.7–98.2
Thermal Conductivity: 25–36 W/m. $^\circ\text{C}$
Thermal Expansion ($10^{-6}/^\circ\text{C}$): 2.8–3.2 over the range of 0–100°C
Electrical Resistivity: $10^{14} \Omega \cdot \text{cm}$
Dielectric Constant @35 GHz: 7.9–8.14
Loss Tangent @35 GHz: 0.0017–0.0006
Vickers Hardness: 16–18 GPa
Weibull Modulus: 15–30 MPa
Fracture Toughness 5–7.5 $\text{MPa}\sqrt{\text{m}}$
Young's Modulus: 260–330 GPa (see Fig. 13.4)
Poisson's Ratio: 0.23–0.27
Flexural Strength: 600–1200 MPa (see Fig. 13.5)

Note: Test temperature is 20°C unless otherwise stated
Material is $\beta\text{Si}_3\text{N}_4$ unless specified

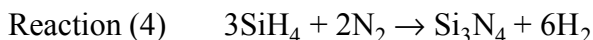
The range of deposition temperature is 755–810°C with a high dilution of nitrogen.^[37] When a high-frequency plasma (13.56 MHz) is used, the deposition temperature is lower (400–600°C).^[38]

A common deposition reaction, used widely in semiconductor processing, combines ammonia with silane as the silicon source:



Deposition temperature ranges from 700 to 1150°C and pressure up to 1 atm. Excess ammonia is used since it decomposes slower than silane. The ammonia-to-silane ratio should be greater than 10/1 over stoichiometric.

Reactions (1), (2) and (3), which all use ammonia, have a tendency to deposit silicon nitride with a high ratio of included hydrogen, especially at the lower temperatures and if a plasma is used. This tendency is often detrimental but it can be remedied, at least to some degree, by using nitrogen instead of ammonia:



However, the nitrogen molecule has a far greater bonding energy than ammonia and is more difficult to dissociate into free atomic nitrogen active species. Consequently, the deposition rate is extremely slow. This can be offset by plasma activation with high frequency (13.56 MHz) or electron cyclotron resonance (ECR) plasmas^{[39]–[42]} and with microwave activation.

Deposition at low temperature (200–400°C) is possible by plasma-CVD from the reaction of ammonia and a metallo-organic precursor: tetrakis(dimethylamido)silicon, $\text{Si}(\text{NMe}_2)_4$. The films are essentially featureless.^[43]

7.3 Applications

The market for silicon nitride is fast growing, particularly in structural and chemical resistance applications and as a thin film in semiconductor devices.^[31]

- Crucibles for silicon single-crystal processing.
- Crucibles and vessels for handling corrosive chemicals and molten metals.
- High-temperature gas-turbine components.
- Diesel-engine components.
- Rotors for turbocharger.
- Cutting tools (Si_3N_4 and Sialons).
- Components for welding, tube drawing, and extruders.
- Ball and roller bearings.
- Bearing seals and check valves.
- Blast nozzles.
- Thermocouple tubes.
- Heat exchangers, pumps, and seal faces.
- Passivation layers, multilayer resist stacks, diffusion barriers, interlevel dielectrics, side-wall spacers, trench masks, oxidation masks, etc., in semiconductor devices.
- Whiskers for high strength reinforcement.

8.0 THE CVD OF TITANIUM NITRIDE

8.1 Characteristics and Properties

Titanium nitride (TiN) is an important industrial material used extensively as a CVD coating. Its characteristics and properties are summarized in Table 10.7.

Table 10.7
Characteristics and Properties of Titanium Nitride

Phase: TiN (major)
Structure and Lattice Parameter: fcc B1 (NaCl), $a = 0.424$ nm
Space Group: Fm3m
Pearson Symbol: cF8
Composition: TiN _{0.6} to TiN _{1.1}
Molecular Weight: 64.95
Color: gold
X-ray Density : 5.40 g/cm^3
Melting Point: 2950°C
Debye Temperature: 636K
Specific Heat (C_p): $33.74 \text{ J/mol}\cdot\text{K}$
Heat of Formation ($-\Delta H_f$) at 298K: $338 \text{ kJ/g-atom metal}$
Thermal Conductivity (K): $19.2 \text{ W/m}\cdot^\circ\text{C}$
Thermal Expansion: $9.35 \times 10^{-6}/^\circ\text{C}$
Electrical Resistivity: $20 \pm 10 \mu\Omega\cdot\text{cm}$
Superconductive Transition Temperature: 5.6 K
Hall Constant: $-0.7 \pm 0.2 \times 10^{-4} \text{ cm}^3/\text{A}\cdot\text{s}$
Magnetic Susceptibility: $+38 \times 10^{-6} \text{ emu/mol}$
Vickers Hardness: 18–21 GPa
Modulus of Elasticity: 251 GPa

Note: Test temperature is 20°C unless otherwise stated

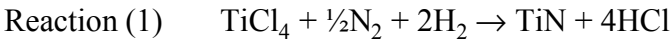
Chemical Resistance. TiN begins to oxidizes in air at approximately 800°C . It is chemically stable at room temperature in the presence of most reagents. It is slowly attacked by concentrated acid solution with rising temperature.

Diffusion Barrier. TiN is an excellent diffusion barrier especially for the aluminum/silicon couple.

8.2 CVD Reactions

Two different chemical systems are presently in development and can be summarized as follows.

Reduction Reactions. Titanium nitride coatings are produced by CVD with titanium tetrachloride as the metal source and either nitrogen gas or ammonia as a source of nitrogen:



The range of temperature for Reaction (1) is 900–1200°C with best results obtained at 1000°C. An argon diluent is used at pressures up to 1 atm.^{[44][45]} Reaction (2) takes place at lower temperature (480–700°C) and is usually carried out at low pressure (≈ 1 kPa) with excess hydrogen.^[46] The ammonia reaction generally has a higher deposition rate, owing to the high reactivity of the monatomic nitrogen released in the ammonia decomposition.

Reaction (1) is also obtained in a high frequency plasma (13.56 MHz) at 150 Pa pressure and at a low deposition temperature of 500°C.

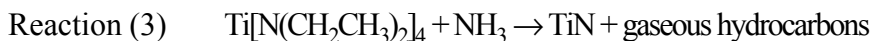
Advantages of the reduction reactions are excellent microstructure free of carbon contamination, and high thermal stability. The disadvantage is the need for relatively high deposition temperatures (ca. 550–700°C).^{[47]–[50]}

Another example of the CVD of TiN is deposition by laser activation using a CO₂ laser with N₂H₂ and TiCl₄ reactant gases. Deposition temperatures are not mentioned but presumed to be low. The composition of the film is substoichiometric (N/Ti < 1).^[51]

Orientation Control of CVD TiN Films. The crystal orientation of TiN deposited by CVD can be controlled by the partial pressure of TiCl₄ to improve the diffusion barrier properties.^[52] The bond

dissociation enthalpies and atomization energies of TiN and Ti(NH) compounds are examined and compared with experimental results of the CVD of TiN from TiCl₄.^[53]

MOCVD Reactions. A great deal of interest has been generated by the availability of two metallo-organic titanium compounds, tetrakis-diethylamino titanium (TDEAT) and tetrakis-dimethylamino titanium (TDMAT). These precursors make possible the deposition of TiN at lower temperature.^{[54][55]} These compounds are liquid at room temperature. A flow of helium bubbling through the warm precursor entrains the vapor into the deposition chamber. Deposition temperature is approximately 320°C. The following reactions occur:



In Reaction (3), the level of impurities (C and O₂) remains high and Reaction (2) is usually preferred, although carbon retention is still a problem. These reactions are being considered for semiconductor applications to replace sputtering since their principal advantage is the low deposition temperature compatible with back-end of line (BEOL) processing compatibility in the fabrication of electronic circuits.^[56]

Using Reaction (4), a thin film of TiN was formed which was then plasma-treated in nitrogen. The coating has low resistivity even after exposure to air after 24 days. This film was successfully applied to sub-half-micron devices.^[57]

Deposition of TiN by the thermal decomposition of tetrakis(dimethylamido)titanium (TDMAT) in a nitrogen atmosphere (as opposed to ammonia) was characterized by a simple Arrhenius rate expression. Adequate deposition rates and good step coverage were achieved for 3/1 aspect ratio holes, 0.40 micron in size. A reactor model was designed.^{[58][59]}

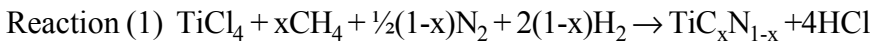
8.3 Applications

CVD titanium nitride (TiN) is the most important interstitial-nitride coating from an application standpoint. It is used extensively to provide wear resistance and as a diffusion barrier and antireflection coating in semiconductor devices.^[60]

- Wear-resistant coatings on cemented carbides, either singly or in combination with TiC, TiCN and Al₂O₃.
- Coatings on tool steel for twist drills.
- Diffusion barriers and anti-reflection coatings in integrated circuits.

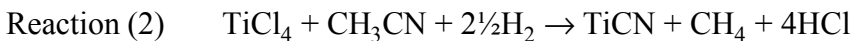
9.0 THE CVD OF TITANIUM CARBONITRIDE

Titanium carbonitride (TiC_xN_{1-x}) combines the wear properties of TiC with the low friction and oxidation- and chemical-resistance of TiN. It is an important material for tool coating. It is deposited by the following simplified reaction:



This reaction is carried out in a hydrogen atmosphere and at a temperature of approximately 1000°C.

If acetonitrile (CH₃CN) is used as a carbon and nitrogen source, the deposition temperature is lower and the process can be used to coat tool steel.^{[61][62]} The reaction is carried out at low pressure and at a temperature range of 700–900°C. It is as follows (in simplified form):



10.0 THE CVD OF OTHER NITRIDES

The following nitrides have been deposited mostly on an experimental basis:[63]

- Gallium nitride (GaN) from the ammonolysis of GaCl_3 .
- Germanium nitride (Ge_3N_4) from the ammonolysis of GeCl_4 .
- Tantalum nitride (TaN) from the metal chloride reaction with nitrogen at 800–1500°C.
- Zirconium nitride (ZrN) from the reaction of ZrCl_4 with nitrogen in hydrogen at 1150–1200°C.

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The CVD of Ceramic Materials: Oxides

1.0 INTRODUCTION

Oxides are the original and largest group of ceramic materials, notable for their chemical inertness, good high temperature properties, and resistance to oxidation. Most oxides have a significant degree of ionic bonding, since oxygen is the most electronegative divalent element. As a result, they generally have the characteristics of ionic crystals, i.e., optical transparency when pure, high electrical resistivity, low thermal conductivity, diamagnetism, and chemical stability. There are notable exceptions; for instance, some oxides such as indium and tin oxides are electrically conductive. Others, such as beryllium oxide, have high thermal conductivity.

The number of oxides is large since most metallic elements form stable compounds with oxygen, either as single or mixed oxides. However, the CVD of many of these materials has yet to be investigated and generally this area of CVD has lagged behind the CVD of other ceramic materials, such as metals, carbides, or nitrides. The CVD of oxides has been slower to develop than other thin-film processes, particularly in optical applications where evaporation,

sputtering, and sol-gel are prominent. This situation is changing and CVD is gradually becoming a major process for oxide deposition (especially for silicon dioxide).

Only those oxides for which CVD information has been reported in the literature and which are of some industrial importance are reviewed here. In this chapter, each of these oxides is listed alphabetically with its basic properties, its major CVD reactions and processes, and its present and potential applications. A more extensive review of applications is given in Chs. 13 to 19.

2.0 ALUMINUM OXIDE

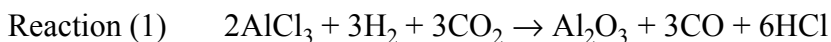
2.1 Characteristics and Properties

Aluminum oxide (Al_2O_3), also known as alumina, is a highly stable compound with many industrial applications. It is readily obtained by CVD. Its characteristics and properties are summarized in Table 11.1.

Chemical Resistance. Alumina is resistant to oxidation and has extremely low permeability to oxygen. It is not attacked by most chemical reagents at room temperature.

2.2 CVD Reactions

A common reaction for the deposition of alumina is the hydrolysis of aluminum trichloride:



This reaction, based on the classic water-gas reaction, takes place in excess hydrogen, at an optimum temperature of 1050°C and at low pressure (ca. 1 Torr).^{[1]–[3]} It is the preferred reaction for tool coatings and electronic applications. The formation of alumina is

dependent on the rate of formation of H_2O , which is the rate-limiting factor. The control of H_2O formation is critical as H_2O and AlCl_3 react rapidly. If the concentration of H_2O is too high, gas phase precipitation results, which leads to a powdery deposit. At 850°C , the alumina is amorphous. It becomes crystalline above 1000°C with a fine, uniform grain structure.

Table 11.1
Summary of Characteristics and Properties of Aluminum Oxide

Composition: Al_2O_3
Molecular Weight: 101.96 g/mol
Color: White
X-ray Density: 3.965 g/cm^3
Crystal structure: rhombohedral, $a = 0.513 \text{ nm}$
Melting Point: 2015°C
Thermal Conductivity ($\text{W/m}\cdot^\circ\text{C}$): 25 to 29 (at full density)
Thermal Expansion ($10^{-6}/^\circ\text{C}$): 7 to 8.3
Electrical Resistivity: $10^{22} \Omega\cdot\text{cm}$
Dielectric Constant: 4.5–8.4 at 1000 cps
Dissipation factor: 0.05 at 1000 cps
Loss factor: 0.5 at 1000 cps
Dielectric Strength: 15 kV/mm
Refractive index: 1.75
Vickers Hardness: 18.73 GPa
Young's Modulus: 378 GPa
Flexural Strength: 421 MPa
Compressive Strength: 3455 MPa

Note: Test temperature is 20°C unless otherwise stated

MOCVD is also used to deposit alumina at lower temperatures than Reaction (1). A common reaction is the pyrolysis of an aluminum alkoxide such as aluminum isopropoxide, $\text{Al}(\text{OC}_3\text{H}_7)_3$. The formation of Al_2O_3 proceeds readily since the energy of the O-C bond (200–300 kJ/mol) is much lower than that of the Al-O bond (ca. 500 kJ/mol). No additional oxygen source is required as the ratio of aluminum to oxygen in the precursor is 1/3. Although decomposition begins at approximately 300°C, it is necessary to operate above 900°C to obtain the temperature-stable $\alpha\text{-Al}_2\text{O}_3$.^[4] The decomposition of aluminum acetylacetonate is also used.^[5]

The decomposition of aluminum alkyls, such as $(\text{CH}_3)_3\text{Al}$ or $(\text{C}_2\text{H}_5)_3\text{Al}$, in an oxidizing atmosphere, such as O_2 or N_2O , produces alumina deposits in a temperature range of 250–500°C.^[5]

2.3 Applications

- Coatings for carbide tools (usually with TiC and TiN underlayers).^[6]
- Sealant coatings for plasma-sprayed oxides.^[7]
- Thin films in the fabrication of transistors (FET) and other semiconductor applications.^[3]

3.0 CHROMIUM OXIDE

3.1 Characteristics and Properties

Chromium oxide (Cr_2O_3), also known as chromia, is a refractory material with excellent corrosion and oxidation resistance. It is produced by CVD mostly on an experimental basis. Its characteristics and properties are summarized in Table 11.2.

Table 11.2
Summary of Characteristics and Properties of Chromium Oxide

Composition: Cr_2O_3
Molecular Weight: 99.99 g/mol
Color: greenish
X-ray Density: 5.21 g/cm^3
Crystal structure: hexagonal
Melting Point: 2265°C
Thermal Conductivity ($\text{W/m}\cdot^\circ\text{C}$): 33
Thermal Expansion ($10^{-6}/^\circ\text{C}$): 9.0
Electrical Resistivity: $1.3 \times 10^3 \Omega\cdot\text{cm}$
Refractive index: 2.55

| Note: Test temperature is 20°C unless otherwise stated |

Chemical Resistance. Chromium oxide has excellent corrosion and oxidation resistance.

3.2 CVD Reactions

Chromium oxide is deposited by the decomposition of chromium acetyl acetonate, $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$, in the $520\text{--}560^\circ\text{C}$ temperature range.^[8] It can also be deposited by the decomposition of the carbonyl in an oxidizing atmosphere (CO_2 or H_2O), at low pressure ($< 5 \text{ Torr}$).^[1]

3.3 Applications

- Intermediate layer in corrosion- and erosion-resistant applications.

4.0 HAFNIUM OXIDE

4.1 Characteristics and Properties

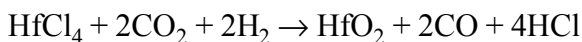
Hafnium oxide (HfO_2), also known as hafnia, is a refractory and stable oxide with extremely low vapor pressure, which is similar in structure and properties to zirconium oxide. It goes through a polymorphic phase change from a monoclinic to a tetragonal structure at 1615°C . This change is accompanied by a volume reduction of approximately 3.4%, resulting in the development of large internal stresses. To avoid this disruption, hafnia is stabilized to form a cubic structure (fluorite) by the addition of a small amount (ca. 10%) of another oxide of cubic symmetry, such as yttria, Y_2O_3 .

The need to stabilize hafnia makes it difficult to deposit this oxide by CVD and CVD has been used so far mostly on an experimental basis. Its characteristics and properties are summarized in Table 11.3.

Chemical Resistance. Stabilized hafnia is resistant to oxidation but is particularly susceptible to oxygen diffusion, through oxygen vacancies in the lattice. In other words, it is not a good oxygen barrier. It is not attacked by most chemical reagents at room temperature.

4.2 CVD Reactions

The most common deposition reaction uses hydrolysis of a metal halide, such as HfCl_4 , in excess hydrogen (the water-gas reaction):^[9]



Optimum deposition temperature is 1000°C and pressure is low (< 20 Torr). The chloride is a solid at room temperature and is preferably generated *in situ*.

Hafnia can also be deposited by the pyrolysis of a metallo-organic such as hafnium acetylacetonate, $\text{Hf}(\text{C}_5\text{H}_7\text{O}_2)_3$, at 400–750°C, or hafnium trifluoro-acetylacetonate, $\text{Hf}(\text{C}_5\text{H}_4\text{O}_2\text{F}_3)_4$, at 500–550°C with helium and oxygen as carrier gases.^[10]

Table 11.3
Summary of Characteristics and Properties of Hafnium Oxide

Composition: HfO_2
Molecular Weight: 210.49 g/mol
Color: grey
X-ray Density: 9.68 g/cm ³ (monoclinic)
Crystal structure: monoclinic or cubic (fluorite) when stabilized
Melting Point: 2015°C
Thermal Conductivity (W/m•°C): 1.67
Thermal Expansion (10 ⁻⁶ /°C): 6.5
Electrical Resistivity: 10 ⁹ Ω•cm
Vickers Hardness: 14.71 GPa
Flexural Strength: 110 MPa
Compressive Strength: 1380 MPa

Note: Test temperature is 20°C unless otherwise stated

4.3 Applications

- Diffusion barrier in semiconductor devices (experimental).
- Oxidation-resistant coatings.
- Wire coating for emitters.

5.0 SILICON DIOXIDE

5.1 Characteristics and Properties

Silicon dioxide (SiO_2), also known as silica, is a major industrial material with many applications particularly in the semiconductor industry in the form of coatings, which are produced mostly by CVD. It is an excellent electrical insulator with very low thermal expansion and good resistance to thermal shock. Its characteristics and properties are summarized in Table 11.4.

Chemical Resistance. Silica is resistant to oxidation and is not attacked by most chemical reagents at room temperature.

Table 11.4
Summary of Characteristics and Properties of Silicon Dioxide

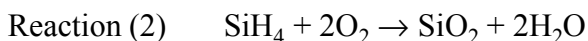
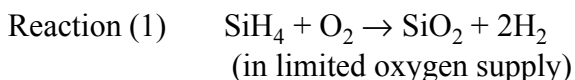
Composition: SiO_2
Molecular Weight: 60.09 g/mol
Color: clear
X-ray Density: 2.20 g/cm ³
Crystal structure: hexagonal
Melting Point: 1610°C (molten SiO_2 has high viscosity)
Thermal Conductivity (W/m•°C): 12
Thermal Expansion (10 ⁻⁶ /°C): 0.5 (0–150°C range)
Electrical Resistivity: 10 ²¹ μΩcm
Dielectric Constant: 3.9 to 4.3 at 1000 cps (depending on process conditions)
Refractive index: 1.46
Vickers Hardness: up to 9 GPa

Note: Test temperature is 20°C unless otherwise stated

5.2 CVD Reactions

Many reactions are being used to deposit silicon dioxide, both experimentally and in production, and many more are being investigated in the laboratory. The selection depends on the application, the temperature limitations, the type of equipment available, and other factors.

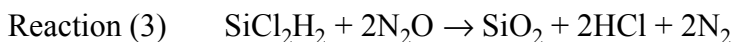
Common deposition reactions are based on the combination of silane with various oxidizers, either as thermal CVD or plasma CVD as follows:^[11]



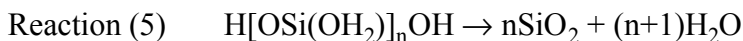
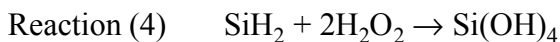
Both reactions may take place simultaneously at a deposition temperature of 450°C and at atmospheric pressure. Reaction (1) can also take place in a plasma at 15–300 mTorr and in a temperature range of 200–300°C with a silane-to-oxygen ratio of 10/1 in a flow of argon or helium. These two reactions are used to produce doped silica by adding a doping gas such as diborane (B₂H₆) or phosphine (PH₃) to the stream.

Another common deposition reaction uses carbon dioxide as the oxygen source in a plasma at temperatures ranging from 200 to 600°C and pressure usually less than 1 Torr.^[12]

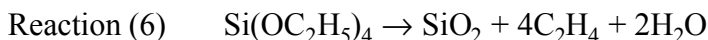
Nitrous oxide (N₂O) is another common oxidizer, which is used with silane in a plasma at 200–350°C, with ratios of N₂O to silane of 15/1 to 30/1.^[13] It is also used with dichlorosilane in a deposition temperature range of 850–950°C and at low pressure (<1 Torr):^[14]



Hydrogen peroxide (H_2O_2) has shown to be an excellent source of oxygen in a plasma. The reaction has several steps beginning by the formation of a gaseous monosilicic acid, followed by polymerization and the removal of H_2O , as follows:^[15]



MOCVD of Silica. Considerable work is being done with the MOCVD of silica, which is rapidly expanding in semiconductor processing. The most common MOCVD reaction is the decomposition of tetraethyl orthosilicate (TEOS), shown in simplified form as follows:^[1]



This reaction normally takes place at 700°C and at low pressure (< 1 Torr). Doping is accomplished by the addition of arsine, diborane, or phosphine. The addition of ozone (O_3) to Reaction (6) at atmospheric pressure or sub-atmospheric pressures provides films with excellent properties.^{[16]–[19]}

Silica is also deposited by the decomposition of diacetoxym-ditertiarybutoxy silane (DADBS) at 450–550°C and low pressure (< 1 Torr) and by the decomposition of octamethyl-cyclotetrasiloxane in ozone at 400°C at low pressure.^{[20][21]}

Fluorinated Silicon Oxide. The introduction of fluorine in the ratio of 2 to 14 at.% lowers the dielectric constant, which is reported as low as 3.0. This is a major factor in the design of dielectric films. The CVD of these fluorinated compounds is accomplished by plasma-CVD and usually with SiF_4 as a fluorine source. Also available are fluorinated compounds, such as fluorotriethoxysilane (FTES), 1,2bis(methyldifluorosilyl)ethane, and 2,5disilahexane.^[22]

5.3 Applications

- Passivation layers, surface dielectric, and doping barriers in semiconductor devices.
- Intermetallic dielectrics.
- Diffusion sources.^[22]
- Etch barriers.
- Oxidation protection of stainless steel in nuclear reactors.^[23]
- Preparation of optical fibers.
- Passivation layers in energy-saving architectural glass (E-glass).
- Barrier layer for SnO₂ films for glass coating.^[24]

6.0 TANTALUM OXIDE

6.1 Characteristics and Properties

Tantalum oxide (Ta₂O₅) has useful optical and dielectric properties. It is readily obtained by CVD with still-limited industrial applications. Its characteristics and properties are summarized in Table 11.5.

Chemical Resistance. Tantalum oxide is resistant to oxidation and is not attacked by most chemical reagent at room temperature.

Table 11.5
Summary of Characteristics and Properties of Tantalum Oxide

Composition: Ta ₂ O ₅
Molecular Weight: 441.89 g/mol
Color: transparent
X-ray Density: 8.27 g/cm ³
Crystal structure: orthorhombic
Melting Point: 1870°C
Dielectric Constant: 25–36 at 1000 cps
Refractive index: 2.1 to 2.2
Vickers Hardness: 12.6 GPa

Note: Test temperature is 20°C unless otherwise stated
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6.2 CVD Reactions

The hydrolysis of tantalum chloride is a common deposition reaction, which is usually carried out in excess hydrogen and in the temperature range of 600–900°C.^[25]



MOCVD reactions are used increasingly, such as the pyrolysis of tantalum ethylate, Ta(OC₂H₅)₅, in oxygen and nitrogen at 340–450°C and at a pressure of <1 Torr. This is followed by an annealing cycle at 600–900°C.^[26] Tantalum is also deposited by the pyrolysis of the tantalum dichlorodiethoxy acetylacetonate at 300–500°C.^[27]

6.3 Applications

- High dielectric-constant capacitors.
- Gate insulators in MOS devices.
- Optical coatings, anti-reflection coatings, and coatings for hot mirrors.

7.0 TIN OXIDE

7.1 Characteristics and Properties

Tin oxide, SnO_2 , has unusual physical properties. It is a good electrical conductor. It is highly transparent to the visible and highly reflective to the infrared spectrum. It is deposited extensively by CVD mostly for optical applications. Its characteristics and properties are summarized in Table 11.6.

Table 11.6
Summary of Characteristics and Properties of Tin Oxide

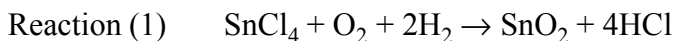
Composition: SnO_2
Molecular Weight: 134.89 g/mol
Color: transparent
X-ray Density: 7.0 g/cm ³
Crystal structure: tetragonal (most common)
Melting Point: 1630°C (decomposes above 1500°C)
Electrical Resistivity: 0.6 $\Omega \cdot \text{cm}$
Refractive index: 2.0 to 2.1

Note: Test temperature is 20°C unless otherwise stated

Chemical Resistance. Tin oxide is resistant to oxidation and is not attacked by most chemical reagents at room temperature.

7.2 CVD Reactions

Tin oxide is deposited with tin chloride as a metal source at 600–800°C, usually at low pressure.^[1]



MOCVD of SnO₂. Tin oxide is obtained by the oxidation of the metallo-organic compound tetramethyl tin at atmospheric pressure or at low pressure (<1 Torr) in the range of 350–600°C, typically 470°C.^{[28]–[30]}

Another MOCVD precursor is dimethyl tin chloride, which is reacted with oxygen at 540°C in the following (simplified) reaction:^[31]



Fluorine doping modifies the optical properties and is accomplished by the addition of CF₃Br in the gas stream. Doping results in a considerable increase in electrical conductivity with a resistivity as low as $5 \cdot 10^{-4} \, \Omega\text{cm}$.^[32]

SnO₂ is codeposited with indium oxide to form a compound known as indium tin oxide (ITO), widely used as a transparent conductive film. ITO is usually deposited by sputtering and little work on CVD has been reported.

7.3 Applications

- Energy saving coatings for plate glass (E-Glass) and light bulbs.^[24]
- Transparent electrodes in photovoltaic cells.

- Transparent heating elements.
- Antistatic coatings.
- Coatings for solar cells.
- Oxygen sensors for air/fuel control in combustion engines (niobium oxide, Nb_2O_5 , is also used for this application).

8.0 TITANIUM OXIDE

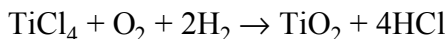
8.1 Characteristics and Properties

Titanium dioxide (TiO_2), also known as titania, is the most common of several known titanium oxides. It is deposited by CVD on an experimental and production basis. Its characteristics and properties are summarized in Table 11.7.

Chemical Resistance. Titanium oxide is resistant to oxidation and is not attacked by most chemical reagents at room temperature.

8.2 CVD Reactions

The oxidation of the chloride is a common deposition reaction. It takes place at 400–1000°C as follows:[25]



MOCVD of Titania. TiO_2 is often produced by the pyrolysis of a titanium alkoxide, such as titanium ethoxide, $\text{Ti}(\text{OC}_2\text{H}_5)_4$, in an oxygen and helium atmosphere at 450°C. Another reaction is based on titanium tetraisopropoxide, $\text{Ti}(\text{OC}_3\text{H}_7)_4$, with oxygen at 300°C and at low pressure (< 1 Torr).[33][34] These precursors have low boiling point (ca. 120°C).

Table 11.7
Summary of Characteristics and Properties of Titanium Oxide

Composition: TiO_2 (most common)
Molecular Weight: 79.90 g/mol
Color: white
X-ray Density: 4.35 g/cm ³
Crystal structure: tetragonal (most common)
 Melting Point: 1850°C (decomposes above 1500°C)
Thermal Conductivity (W/m•°C): 8
Thermal Expansion (10 ⁻⁶ /°C): 9.0
 Electrical Resistivity: insulator
 Refractive index: 2.6 to 2.9 (rutile form)

Note: Test temperature is 20°C unless otherwise stated.

8.3 Applications

The applications of titanium oxide are mostly optical and include the following:

- High-index films in multilayer interference filters.
- Antireflection coatings, optical waveguides and photoelectrochemical cells.
- Dielectric layers in thin-film capacitors.

9.0 ZIRCONIUM OXIDE

9.1 Characteristics and Properties

Zirconium oxide (ZrO_2), also known as zirconia, is a refractory material which is similar to hafnia. It goes through three solid polymorphic phase changes from monoclinic to tetragonal at 1170°C and to cubic at 2370°C . The cubic phase has a fluorite crystal structure (open cubic). The monoclinic-to-tetragonal change is accompanied by a large volume reduction of approximately 7.5% resulting in considerable stresses.

To avoid this phase change, zirconia is stabilized in the cubic phase by the addition of a small amount of a divalent or trivalent oxide of cubic symmetry, such as MgO , CaO , or Y_2O_3 . The additive oxide cation enters the crystal lattice and increases the ionic character of the metal-oxygen bonds. The cubic phase is not thermodynamically stable below approximately 1400°C for MgO additions, 1140°C for CaO additions, and below 750°C for Y_2O_3 additions. However, the diffusion rates for the cations are so low at these *subsolidus* temperatures that the cubic phase can easily be quenched and retained as a metastable phase. Zirconia is commercially applied by thermal spray. It is also readily produced by CVD, mostly on an experimental basis. Its characteristics and properties are summarized in Table 11.8.

Chemical Resistance. Zirconia lumina is resistant to oxidation and chemically resistant at low temperature.

Oxygen Diffusion. Stabilized zirconia, with its simple open cubic structure, is particularly susceptible to oxygen diffusion through oxygen vacancies. The addition of 9 mol% Y_2O_3 produces 4.1% vacancies and an ionic conductivity of 300–500 ohm-cm at 1000°C . This ionic conductivity is used in oxygen sensing and in heating-element applications.

Table 11.8
Summary of Characteristics and Properties of Zirconium Oxide

Composition: ZrO_2
Molecular Weight: 123.11 g/mol
Color: white
X-ray Density: 5.56 g/cm³
Crystal structure: monoclinic (see above)

Melting Point: 2677°C
Thermal Conductivity (W/m•°C): 3
Thermal Expansion (10⁻⁶/°C): 10

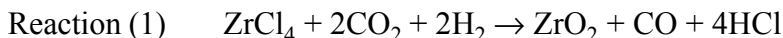
Electrical Resistivity: $1 \times 10^{12} \mu\Omega \cdot \text{cm}$
Refractive index: 2.17 to 2.20

Vickers Hardness: 16 GPa
Young's Modulus: 207 GPa
Flexural Strength: 900–1250 MPa

Note: Test temperature is 20°C unless otherwise stated

9.2 CVD Reactions

Unstabilized zirconia is deposited by the reaction of the metal halide with CO_2 and hydrogen (the water-gas reaction) at 900–1200°C:[¹]



Attempts to deposit yttria-stabilized zirconia by combining Reaction (1) and a similar hydrolysis of YCl_3 as source of yttrium at 700–1000°C were inconclusive.^[35] Codeposition from the chlorides in oxygen at 1100°C has been claimed.^[36]

MOCVD of Zirconia. Ytria-stabilized zirconia is also deposited by MOCVD.^[37] Deposition can be accomplished by the co-decomposition of the tetramethyl heptadiones of zirconium and yttrium, $\text{Zr}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$ and $\text{Y}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$, at 735°C. Deposition is also achieved by the decomposition of the trifluoro-acetylacetonates in a helium atmosphere above 300°C.^[38] Other potential MOCVD precursors are bis(cyclopentadienyl)zirconium dichloride, $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$, and zirconium (IV) trifluoroacetylacetonate, $\text{Zr}(\text{C}_5\text{H}_4\text{O}_2\text{F}_3)_4$.

9.3 Applications

- Electrolytes, oxygen sensors, fuel cells, electronic conduction coatings, and furnace elements.
- Piezoelectricity devices, PLZT ceramics.
- High-temperature passivation of microelectronic devices.
- Structural composites.

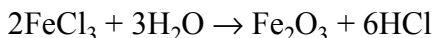
10.0 OTHER OXIDES

The CVD of the oxides described in this section have been only cursorily investigated, yet these materials have interesting properties and many potential applications.

10.1 Iron Oxide

The oxide of trivalent iron, Fe_2O_3 , has a cubic structure, a density of 5.2 g/cm³, a melting point of 1565°C, and a refractive index of 3.0. It is an optical material. It is formed by CVD mostly on an experimental basis.

Iron oxide is deposited by the reaction of a halide, such as iron trichloride, with water at a temperature range of 800–1000°C and at low pressure.^[1]



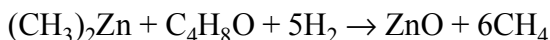
It can also be deposited by MOCVD by the decomposition of the acetylacetonate, $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$, at 400–500°C, or of the iron trifluoro-acetylacetonate, $\text{Fe}(\text{F}_3\text{C}_5\text{H}_4)_3$, at 300°C in oxygen.^[25]

Another MOCVD reaction uses a microwave plasma to decompose iron cyclopentadienyl, $(\text{C}_5\text{H}_5)_2\text{Fe}$, in an oxygen atmosphere in a temperature range of 300–500°C and at low pressure (1–20 Torr).^[39]

Potential CVD applications are beam splitter and interference layer in optical devices and detector for ethyl alcohol.

10.2 Zinc Oxide

Zinc oxide (ZnO) has useful piezoelectric properties. It has an hexagonal structure (wurtzite type) with a density of 5.66 g/cm³. It is relatively unstable and decomposes above 1700°C, which is below its melting point (1975°C). It is readily attacked by all common acids and bases. It has limited CVD applications at this time. It is deposited by MOCVD, with an alkyl precursor, such as dimethyl zinc and tetrahydrofuran (THF).^[40]



The deposition temperature range is 300–500°C, the partial pressure of the alkyl is 0.5–2.5 Torr, and that of THF is 20–80 Torr. ZnO has found applications in piezoelectric devices, transducers, coatings for photoconductive devices, and non-linear resistors (varistors), and overvoltage protectors.

11.0 MIXED OXIDES AND GLASSES

Many mixed oxides can be produced by CVD and the potential number of combinations is large. In this section, some of the most common mixed oxides are reviewed.

11.1 Titanates

The titanates are an important group of mixed oxides with unusual optical, electrical, and mechanical properties. Many of these materials can be deposited by CVD, and CVD may soon become an economical production process.^[41] The most important titanates are as follows.

PZT (lead zirconate titanate) and PLZT (lead lanthanum zirconate titanate) combine ferroelectric, optical, and electronic properties and are used in optoelectronic and piezoelectric devices. Powders for hot pressing produced by CVD are being investigated.

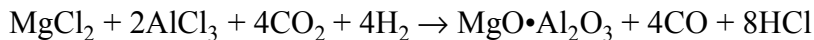
Lead titanate (PbTiO_3) is a ferroelectric material with unusual pyroelectric and piezoelectric properties. It is deposited by MOCVD from ethyl titanate and lead vapor in oxygen and nitrogen at 500–800°C.^[42]

Another ferroelectric material is bismuth titanate, ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$), which is deposited from triphenyl bismuth, $\text{Bi}(\text{C}_6\text{H}_5)_3$, and titanium isopropoxide at low pressure (5 Torr) and at temperatures of 600–800°C.^[43]

Strontium titanate (SrTiO_3) has a large dielectric constant of 12, and a high refractive index with potential opto-electronic applications. It is deposited by MOCVD from titanium isopropoxide and a strontium beta-diketonate complex at 600–850°C and 5 Torr.^[44]

11.2 Magnesia Aluminate (Spinel)

Magnesia aluminate (MgAl_2O_4) is deposited by combining the two metal chlorides with CO_2 and H_2 at 950°C as follows:^[45]



A potential application is as an insulator coating on silicon in semiconductor devices.

11.3 Glasses

Glasses are oxides which have hardened and become rigid without crystallizing. The glassy structure consists of silica tetrahedra or other ionic groups that provide a solid, non-crystalline structure.

A widely used glass is phosphosilicate (PSG), which is used extensively in semiconductor devices as a passivation and planarization coating for silicon wafers. It is deposited by CVD by the reaction of tetraethylorthosilicate (TEOS): $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$, and trimethylphosphate: $\text{PO}(\text{OCH}_3)_3$, in a molecular ratio corresponding to a concentration of 5 to 7% P. Deposition temperature is usually 700°C and pressure is 1 atm.

Borophosphosilicate glass (BPSG) provides a lower reflow temperature (800°C) than PSG and is used increasingly. It is deposited by reacting tetraethylorthosilicate, trimethylphosphite, and trimethylborate with oxygen. Another reaction uses the hydrides, i.e., silane (SiH_4), phosphine (PH_3), and diborane (B_2H_6), with nitrous oxide (N_2O). The respective amount of boron and phosphorus in the deposit is approximately 5% by weight. These reactions take place by thermal CVD either at atmospheric or at low pressure. However, the use of plasma CVD at low pressure (3–10 Torr) is rapidly increasing due to the advantageous lower deposition temperature (355°C).^{[46][47]} BPSG is used extensively as an interlayer dielectric on polysilicon.

12.0 OXIDE SUPERCONDUCTORS

The deposition of thin films of the high-temperature superconductor yttrium-barium-copper oxide, $\text{YBa}_2\text{Cu}_3\text{O}_7$, is obtained from the mixed halides, typically YCl_3 , BaI_2 , and CuCl_2 , with O_2 and H_2O as oxygen sources. Deposition temperatures are 870–910°C.^[48]

$\text{YBa}_2\text{Cu}_3\text{O}_7$ films are also obtained by MOCVD from a mixture of acetylacetonates (tetramethyl heptadionate) of yttrium, barium, and copper, typically at a pressure of 5 Torr and at a deposition temperature of 825°C.^{[49][50]} These precursor materials are readily prepared and are available commercially.^[51]

Few commercial applications have reached the market place at this time.^[52]

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12

The CVD of Ceramic Materials: Borides, Silicides, III–V Compounds and II–VI Compounds (Chalcogenides)

1.0 BORIDES

1.1 General Characteristics and Properties

Although boron forms borides with many elements, only the borides of the transition metals have been investigated extensively for their CVD characteristics. Boron forms stable borides with the transition metals, and the most refractory of these and those with the greatest potential interest are the borides of the elements of Groups IVa (Ti, Zr, Hf), Va (V, Nb, Ta) and, to a lesser degree, VIa (Cr, Mo, W) (see Table 9.1 of Ch. 9). Other borides, such as lanthanum and cerium hexaborides (LaB_6 and CeB_6), are of great interest particularly as thermionic emitters but little, if anything, has been reported on their CVD.

The refractory-metal borides have a structure which is dominated by the boron configuration. This clearly favors the metallic properties, such as high electrical and thermal conductivities and high hardness. Chemical stability, which is related to the electronic

structure of the metal, decreases from the borides of the metals of Group IVa to those of Group VIa. Thus, the most stable borides are TiB_2 , ZrB_2 , and HfB_2 . Properties of interest are summarized in Table 12.1.^[1]

Table 12.1
Properties of the Borides

Boride	Density g/cm ³	Melting Point Point°C	Hardness Kg/mm ² (VHN50)	Electrical Resistivity μohm-cm	Thermal Conduc. w/cm•°C	Thermal Expans. 10 ⁻⁶ /°C (300– 1000°C)
HfB ₂	11.20	3250	2900	10–12		6.3–6.8
Mo ₂ B ₅	7.48	2100	2350	18–40		
NbB ₂	7.21	3050	2200	12–65	0.17	5.5–9.2
TaB ₂	12.60	3200	2500	14–68	0.11	5.8–7.1
TiB ₂	4.52	2980	3370	9–15	0.25	6.6–8.6
W ₂ B ₅	13.10	2300	2660	21–56		
ZrB ₂	6.09	3040	2300	7–10	0.25	6.6–6.8

The borides listed above can all be produced by CVD. With a few exceptions, they have found only limited industrial applications so far, in spite of their excellent properties of hardness, erosion resistance, and high-temperature stability.

1.2 Boriding

Boriding by CVD is a relatively simple process whereby a layer of boron is deposited on a metal substrate, followed by heat treatment.^[2] The boron can be deposited by the hydrogen reduction

of the chloride or by the decomposition of diborane (see Ch. 6, Sec. 1.0). During heat treatment, the metal boride is formed by solid-state diffusion of the boron atoms into the metal lattice to form an interstitial compound. This occurs readily since that the atomic radii of the metals are considerably larger than that of the boron (1.17 Å for boron, 2.0 Å for titanium, and 2.16 Å for zirconium).

The rate of boride formation by diffusion increases when going from the metals of Group IVa to those of Group VIa.^{[3][4]} This rate is also related to the stability of the borides; the most stable are those of Group IVa (TiB₂, ZrB₂, and HfB₂) which are the slowest to form while boriding of tungsten (Group VIa) occurs much more rapidly. This swift conversion to tungsten boride is an important factor in the industrial production of boron filaments by CVD (see Ch. 19).

Boriding is used extensively on steel. The reaction occurs with a high hydrogen dilution of the BCl₃ to prevent substrate attack. An iron boride is formed.^[5] Not all metals, however, are suitable to boriding. For instance, the boriding of titanium by CVD in a chloride-based system is more difficult since the titanium substrate is highly susceptible to HCl attack and the rate of diffusion is low.

1.3 Direct Boride Deposition

Unlike boriding, direct boride deposition does not require a reaction with the substrate to form the boride. Both boron and metal atoms are supplied as gaseous compounds.

Borides of Group IVa. TiB₂, ZrB₂, and HfB₂ are readily deposited by the hydrogen reduction of the metal halide, usually the chloride. A typical reaction is as follows:

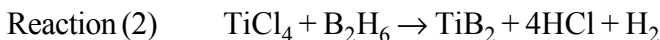


ZrB₂ and HfB₂ are deposited by similar reactions. These reactions take place over a pressure range of a few Torr to 1 atm and

a temperature range of 800–1100°C, in a hydrogen atmosphere.^{[6][7]} A large amount of HCl is produced which may attack the substrate, particularly if it is a metal. This can be avoided by first depositing a barrier layer such as titanium nitride (TiN).^[8]

TiB₂ powder is produced by Reaction (1) in a plasma arc with excess hydrogen. A chlorinated hydrocarbon is introduced in the reaction to generate a small amount of carbon. The carbon assists subsequent densification of the powder by inhibiting grain growth of the TiB₂.^[9]

The Group IVa borides can also be deposited with diborane as a boron source in a pressure range of a few Torr to 1 atm as follows:



The applicable temperature range is lower than that of Reaction (1), 600–1000°C, but free boron tends to be incorporated in the deposit below 650°C.^[10] ZrB₂ is deposited by a similar reaction.^[11]

Borides of Group Va. The borides of Group Va, Nb₂, and TaB₂, are more difficult to deposit than those of Group IVa, since the incorporation of free metal in the deposit is difficult to avoid. However, relatively pure deposits can be obtained by the co-reduction of the bromides at high temperatures (1500°C) and low pressure, or by the co-reduction of the chlorides if the molar gas mixture is preheated to 700–800°C just before entering the reactor.^{[12]–[14]} The incorporation of free metal can also be eliminated by using diborane as a boron source. Deposits of metal-free TaB₂ were obtained in this manner at 500–970°C.^[15]

Borides of Group VIa. As with the borides of Group Va, the incorporation of free metal in the Group VIa borides is difficult to avoid. Both tungsten and molybdenum borides are obtained at high temperature by the hydrogen reduction of the mixed bromides.^[16] Boriding appears a more effective method to form these borides in thin layers (see Sec. 2.2 above).

In addition to the thermal CVD reactions described above, a glow discharge plasma at 480–650°C has been used to deposit TiB₂ from the mixed chlorides.^[17]

1.4 Applications

- Experimental TiB_2 coatings for cemented carbide cutting tools and other wear- and erosion-resistant applications (pumps, valves, etc.).^{[18][19]}
- ZrB_2 coatings for solar absorption.^[20]
- TiB_2 coatings for electrodes for aluminum production (Hall-cell cathodes). TiB_2 has high resistance to molten aluminum yet it is readily wetted by the molten metal and good electrical contact is assured.
- Production of TiB_2 powder for hot-pressing.^[9]

2.0 SILICIDES

2.1 Characteristics and Properties

Silicides are useful compounds characterized by their refractoriness and high electrical conductivity. There are many silicides, since silicon reacts with most metals and often more than one silicide is formed. For instance, there are five known tantalum silicides.

The silicides of major industrial importance are the disilicides of the refractory metals: molybdenum, tantalum, titanium, tungsten, vanadium, and zirconium.^{[21][22]} These compounds are of great interest particularly to the semiconductor industry because of their low electrical resistivity and their ability to withstand high processing temperatures. Silicide properties are listed in Table 12.2.

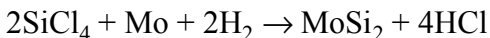
Table 12.2
Selected Properties of Silicides

Property	MoSi ₂	TaSi ₂	TiSi ₂	WSi ₂	ZrSi ₂
Density g/cm ³	6.24	9.08	4.10	9.75	4.90
Structure	tetra- gonal	hexa- gonal	ortho- rhombic	tetra- gonal	ortho- rhombic
Melting Point, °C	2050	2200	1540	2165	1600
Thermal Conductivity W/cm·°C	0.49	0.38	0.46	0.48	0.15
Thermal Expansion ppm/°C (0–1000°C)	8.4	9.0	10.7	7.0	8.7
Electrical Resistivity μohm-cm	40–100	35–70	13–16	30–100	35–40
Oxidation Resistance	excellent	poor	good	poor	poor

2.2 Siliconizing

An older process to form silicides is “siliconizing” which is a relatively simple CVD process used to provide oxidation and chemical resistance to refractory metals. The siliconizing reaction uses the substrate itself, (such as Mo or Ti), as the metal source. Silicon diffuses readily in

these metals at relatively low temperature and the silicide is formed either by a displacement or by a hydrogen-reduction reaction. A typical reaction is the siliconizing of molybdenum as follows:



The deposition temperature is above 1200°C and the deposit usually consists of an outer layer of MoSi_2 and an intermediate layer of MoSi .^{[2][23]} Such reactions are difficult to control and often result in mechanical stresses and voids at the interface, which may cause adhesion failure. The direct deposition of the silicide is often preferred. This is accomplished by reacting a gaseous silicon compound with a gaseous metal compound, as shown in the following sections.

2.3 Molybdenum Disilicide

Oxidation Resistance. Molybdenum disilicide (MoSi_2) is unusual among silicides because of its outstanding oxidation resistance. In the presence of air at high temperature, MoSi_2 oxidizes to form an adherent, non-porous surface layer, which has been tentatively identified as alpha-cristobalite as the principal constituent with other minor but essential phases of SiO_2 or Mo-Si-O ternary compounds. This surface layer acts as an efficient oxygen barrier and eliminates or, at least considerably reduces, further oxidation. Thus oxidation of MoSi_2 is minimized up to approximately 1900°C, which is close to its melting point.

CVD Reactions. MoSi_2 is usually deposited by the reaction of a molybdenum halide with silane. The simplified reactions are as follows:^{[24][25]}



Deposition temperature from the fluoride is 250–300°C at a pressure of < 2 Torr. Deposition temperature from the chloride is 650–950°C at low pressure. In Reactions (1) and (2)—and in other silicide deposition reactions as well—the silane gas is usually highly diluted with an inert gas such as argon.

Also under investigation are MOCVD reactions from precursors having silicon-metal bonds such as $\text{SiH}_3\text{Mo}(\text{CO})_3$.^[26]

2.4 Applications

- Conductive coatings in semiconductor devices.
- Oxidation-resistant coatings.
- Heating elements for high-temperature furnaces in oxidizing atmosphere.

2.5 Tantalum Disilicide

Tantalum disilicide, TaSi_2 , is very refractory and chemically resistant. It is deposited from the reaction of the chloride, TaCl_5 , with silane (SiH_4), or dichlorosilane (SiH_2Cl_2), the latter precursor being preferred. The reaction takes place in a plasma as follows:^[27]



Pressure is low (1–2 Torr) and amorphous deposits are obtained in the temperature range of 400–540°C.

2.6 Applications

- Gate material in VLSI technology.

2.7 Titanium Disilicide

Titanium disilicide (TiSi_2) has very low electrical resistivity and is a promising metallization material.^[28] It is deposited by the following reaction:^[29]

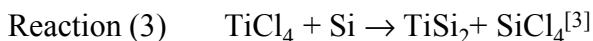


A similar reaction uses dichlorosilane as the silicon source:



Deposition temperature is 800°C and either atmospheric pressure or low pressure is used. This reaction can also be carried out in a plasma at very low pressure and at much lower temperature (450°C).^[30]

A silicon substrate, such as the silicon wafer itself or a thin predeposited layer of silicon, may be used as the silicon source with the following reaction:^{[31][32]}



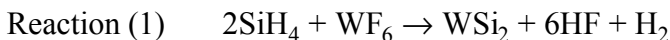
Deposition temperature is 850°C and pressure is < 1 Torr. The reaction is self-limiting since it relies on the diffusion of Si through the silicide.

2.8 Applications

- Schottky barriers and ohmic contacts in IC's.
- Replacement of doped silicon in MOS devices where silicon resistivity (300 $\mu\text{ohm-cm}$) is too high.
- General metallization.

2.9 Tungsten Disilicide

Tungsten disilicide (WSi_2) is refractory and stable with low resistivity. As with other silicides, a common deposition system uses silane as the silicon source with tungsten hexafluoride as follows:^[33]



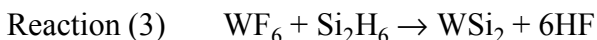
This reaction is usually carried out at 350°C and at low pressure (<1 Torr) with a high ratio of SiH_4 to WF_6 .

Reaction (1) is being replaced by a reaction where dichlorosilane is the silicon source. This provides better conformity and less cracking and peeling:^{[34][35]}



Deposition temperature is in the range of 400–650°C and pressure is < 1 Torr, with a high ratio of SiH_2Cl_2 to WF_6 .

Another deposition reaction uses disilane as the silicon source at atmospheric pressure and at a deposition temperature of 290–300°C, with nitrogen and hydrogen dilution as follows:^[36]



2.10 Applications

- Replacement for polysilicon gates and interconnects in MOS devices.
- Polycide structures (WSi_2 + polysilicon).
- Adhesion layer with non-selective tungsten.

2.11 Other Silicides

Several other silicides of potential interest are the object of active CVD development.

- Cobalt disilicide is deposited from the carbonyl $\text{Co}_2(\text{CO})_8$ at 200°C in vacuum, followed by annealing at 700°C .^[37] It is also deposited from the pyrolysis of $\text{SiH}_3\text{Co}(\text{CO})_4$ at 500°C .^[26]
- Iron disilicide is deposited from $(\text{SiH}_3)_2\text{Fe}(\text{CO})_4$ at 500°C .^[26]
- Niobium silicide (NbSi_3) is deposited by the silane reaction with niobium chloride.^[38] It has an A15 structure and is a superconductor.
- Vanadium silicide, (VSi_2), is deposited from the chlorides (VCl_4 and SiCl_4) at $1000\text{--}1200^\circ\text{C}$ and at 0.25 atm.^[39]

3.0 III–V COMPOUNDS

3.1 Characteristics and Properties

The III–V compounds combine the elements of Group III (aluminum, gallium, indium) with those of Group V (phosphorus, arsenic, antimony, bismuth). As can be imagined, a wide variety of compounds can be produced which, in addition to the binary materials, also include ternary and even quaternary materials.

These materials are useful semiconductors and have a wide range of industrial applications, particularly in opto-electronics. One of their attractive features is the possibility of tailoring the band gap and the lattice constant in the ternary alloys by varying the composition. CVD is now a major production process of these materials.

The III–V compounds now being produced by CVD include: GaAs, GaN, GaP, InAs, InP, AlAs, BP, InGaAs, AlInAs, AlGaAs, GaPAs, InGaN, and InGaPAs. The most common is gallium arsenide (GaAs), which has excellent semiconductor characteristics.^[40]

Its properties are summarized in Table 12.3.

Table 12.3
Properties of Gallium Arsenide at 25°C

Crystalline form: cubic close pack (zinc blende)

Lattice parameters: $a_0 = 0.56531 \text{ nm}$

Melting point, °C: 1510

Density, g/cm³: 5.316

Thermal conductivity, W/m•K: 370

Electrical resistivity, $\mu\Omega\text{m}$: 3×10^8

Bandgap at 300K (eV): 1.43

Saturated Drift Velocity (cm/sec): 2.0×10^7

Drift Mobility

Electrons (cm/V•sec): 8500

Holes (cm/V•sec): 400

Breakdown Electric Field (V/cm): 4×10^5

Dielectric constant: 12.8

Maximum Junction Temperature (°C): ≈ 300

Coherent-light emitter

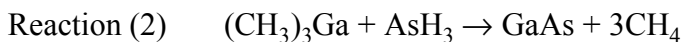
High resistance to radiation

3.2 CVD Reactions

The CVD of the III–V compounds is usually obtained by reacting an alkyl of a Group-IIIb element with a hydride of a Group-Vb element. These reactions have largely replaced the co-reduction of the halides.^[41] The general reaction is as follows:



A specific example is:



These reactions usually occur at atmospheric pressure and in the following temperature range:

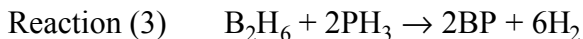
- 650–730°C for GaAs.
- 650–700°C for GaP.
- 630–750°C for InGaAs.
- 700–800°C for AlGaAs.

The molar ratio of the III compound to the V compound is typically 1/10.^[42] To obtain the desired semiconductor properties, dopants are added such as zinc (from diethyl zinc) or magnesium (from bis(cyclopentadienyl) magnesium) for p doping, and silicon (from silane) or selenium (from hydrogen selenide) for n doping.

Arsine (AsH_3) and phosphine (PH_3) are extremely toxic, so less hazardous substitutes such as tertiary butyl arsine, $\text{C}_4\text{H}_{11}\text{As}$, and tertiary butyl phosphine, $\text{C}_4\text{H}_{11}\text{P}$, are being considered.^[43]

Plasma CVD and thermal laser CVD are also used particularly in the deposition of GaAs. The formation of epitaxial GaAs at 500°C and polycrystalline GaAs at 185°C has been reported.^[44]

The reaction of the hydrides of both the Groups IIIb and Vb elements is also used notably in the production of boron phosphide at 950–1000°C as follows:[45]



3.3 Applications

- Microwave devices.[46]
- Photo-chemical cells.[47]
- Light emitting diodes (LED).
- Solid state neutron detector of boron phosphide which is a refractory semiconductor with a wide band gap.[45]
- Field effect transistors (FET) of epitaxial InP.
- Heterostructure bipolar transistors (HBT) of InGaAs and InAlAs.
- BP whiskers.[48]

These and other applications are reviewed in detail in Chs. 13 and 15.

4.0 II–VI COMPOUNDS (CHALCOGENIDES)

4.1 Characteristics and Properties

The chalcogenides are binary compounds of a chalcogen (i.e., the elements of Group IIb: zinc, cadmium, mercury) with a less electropositive element, such as those of Group VIb (oxygen, sulfur, selenium, and tellurium). This section covers the sulfides, selenides, and tellurides. Oxides are reviewed above in Ch. 11. Most of the chalcogenides have useful optical characteristics and their applications are usually found in optics.

The II–VI compounds now being produced by CVD include: ZnSe, ZnS, ZnTe, CdS, HgTe, CdMnTe, and HgCdTe. CdTe, ZnS, and ZnSe are the most important from an industrial standpoint. Selected properties of these three chalcogenides are summarized in Table 12.4.

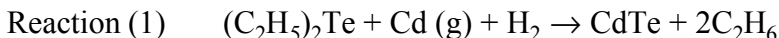
Table 12.4
Properties of Selected Chalcogenides

Property	CdTe	ZnSe	ZnS
Structure	cubic	cubic	hex. (ZnS)
Density, g/cm ³	5.85	5.27	4.09
Melting point, °C	1092	1520	1830
Hardness Knoop, kg/mm ²	45	100–150	250–350
Thermal conductivity W/cm•°C at 25°C	0.41	0.13	0.15
Thermal expansion ppm/°C at 0–450°C	6.2	7.6–8.2	7.5–7.8
Index of refraction at 10.6 μm	2.67	2.40	2.20
Useful bandpass absorption < 0.05 cm in μm		0.6–14	1–5, 7–10
Mechanical properties	low	low	medium

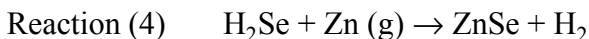
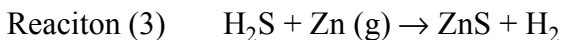
Note: Zinc sulfide (ZnS) has higher mechanical properties and better erosion resistance than zinc selenide but its optical transmission is not as good.

4.2 CVD Reactions

The metals of group IIb (Zn, Cd, Hg) have low vaporization temperatures (Zn: 907°C, Cd: 756°C, Te: 990°C). This favors the reaction of the vaporized metal with an alkyl of the group VI element at a temperature range of 325–350°C, as shown in the following examples:



Other II–VI compounds are deposited by the reaction of the Group VIb hydride with the Group IIb vaporized metal:^[49]



Both reactions occur at 600–800°C and at pressures <100 Torr.

Deposition of CdTe is obtained by the direct combination of the vapors of the two elements which are carried in a stream of hydrogen or helium. CdTe is also deposited by the following MOCVD reaction:^{[49][50]}



Reaction (5) is activated by an excimer laser (K_2F) at a substrate temperature of 150–250°C.

ZnSe is deposited by the reaction of hydrogen selenide with zinc vapor transported in argon, at a deposition temperature of 700–750°C and at a pressure < 100 Torr:^[51]



ZnS is deposited by a reaction similar to Reaction (6) with hydrogen sulfide as the hydrogen source:^{[49][51]}



Deposition temperature is 600–800°C, pressure is 30–40 Torr, and the ratio $\text{H}_2\text{S/Zn}$ is 0.5–0.7.

4.3 Applications

- Infrared transparent windows (ZnS, ZnSe, and ZnTe).
- Photoconductors (CdSe and CdS).
- Photovoltaic devices (CdTe).^[52]
- Windows for CO₂ lasers (ZnS).
- Thin film photovoltaic devices (CdTe is a direct bandgap semiconductor with a bandgap energy of 1.5 eV at room temperature).

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CVD in Electronic Applications: Semiconductors

1.0 INTRODUCTION

The start of the solid-state electronic industry is generally recognized as 1947 when Bardeen, Brattain, and Shockley of Bell Telephone Laboratories demonstrated the transistor function with alloyed germanium. The first silicon transistor was introduced in 1954 by Texas Instruments and, in 1956, Bell Laboratories produced the first diffused junction obtained by doping. The first-solid state transistor diodes and resistors had a single electrical function and were (and still are) known as discrete devices.

A major development in semiconductor technology occurred in 1959 when several components were placed on a single chip for the first time at Texas Instruments, inaugurating the era of integrated circuits (IC's).^[1] Since then, the number of components has increased to the point where, in the new ultra-large-scale-integration designs (ULSI), more than a million components can be put on a single chip. This has been accompanied by a considerable increase in

efficiency and reliability and a better understanding of the related physical and chemical phenomena.

The result of these developments was a drastic price reduction in all aspects of solid-state circuitry. The cost per unit of information (bit) has dropped by an estimated three orders of magnitude in the last twenty years.

Obversely, this dramatic progress has led to a considerable increase in the complexity of the manufacturing technology and the need for continuous efforts to develop new materials and processes in order to keep up with the ever-increasing demands of circuit designers.

These advances are due in a large part to the development of thin-film technologies such as evaporation, sputtering, and CVD. The fabrication of semiconductor devices is a complicated and lengthy procedure which involves many steps including lithography, cleaning, etching, oxidation, and testing. For example, a 64 Mb DRAM, scheduled for 1997 production, requires 340 processing steps.

Many of these steps include CVD, and CVD is now a major process in the fabrication of monolithic integrated circuits (IC), custom and semi-custom ASIC's, active discrete devices, transistors, diodes, passive devices and networks, hybrid IC's, opto-electronic devices, energy-conversion devices, and microwave devices.

2.0 ELECTRONIC FUNCTIONS AND SYSTEMS

In order to obtain a clear view of the role of CVD in the technology of the electronic industry, it is important to have an understanding of the various electronic functions and systems.

2.1 Conductors, Semiconductors, and Insulators

An electric current can be defined as a flow of electrons. In conductors, such as metals, the attraction between the outer electrons and the nucleus of the atom is weak, the outer electrons can move readily and consequently metals are good conductors of electricity. In other materials, electrons are strongly bonded to the nucleus and are not free to move. Such materials are insulators (or dielectrics). In semiconductors, the conductivity falls between those of conductors and insulators. Table 13.1 lists the characteristics of all three groups.

Table 13.1
Electrical Characteristics of Materials

Device	Typical material	Electron mobility	Resistivity ohm-cm
Conductor	Copper Silver Gold Tungsten Silicides	Free to move	10^{-5} to 10^{-6}
Semiconductor	Silicon Germanium III–V & II–VI compounds Diamond Silicon carbide	Partially able to move	10^{-2} to 10^9
Insulator (dielectrics)	Alumina Silicon oxide Silicon nitride Glass	Bound to nucleus	10^{12} to 10^{22}

2.2 Categories of Electronic Devices

Electronic devices are either discrete devices or integrated circuits (IC's). Discrete devices perform a single function and include the following:

- *Transistors*, which control the current through a junction of semiconductor materials by a voltage signal from an emitter electrode.
- *Resistors*, which are passive devices limiting the flow of electrical current in proportion to the applied voltage and usually made of tantalum, nichrome, titanium, or tungsten.
- *Thermistors*, which are resistors made of semiconductor material having a resistance that varies rapidly and predictably with temperature.
- *Capacitors*, which store an electric charge and consist of two conductors usually made of tantalum, titanium, nichrome, platinum, or gold, separated by a dielectric, usually made of silica or silicon nitride.

Integrated circuits (IC's) are circuits in which bipolar transistors, field-effect transistors (FET), resistors, capacitors, and their required connections are combined on a single chip of semiconductor material which is usually made of single-crystal silicon.

2.3 Modern Circuit Characteristics

The characteristics of modern integrated circuits can be summarized as follows:

- Feature geometry is continuously decreasing in size. It now routinely reaches 0.25 μm in production and is scheduled to be less than 0.15 to 0.20 μm in the year 2000.

- With reduction in size comes reduction in intrinsic switching time and proportionally higher device speed. Present design speed is in the range of 100 MHz and is expected to reach 300 MHz or higher by the year 2000.
- Power consumption is to be further reduced.
- Reduction in resistive and capacitive (RC) delays is continuing by the use of higher conductivity materials and improved ohmic contact.

2.4 Three-Dimensional Structures

The switching speed of a transistor is limited by the time required by an electron to move across the length of the device (the gate in an FET or the base in a bipolar transistor). Moving across the thickness, in addition to parallel to the surface, would greatly reduce the switching time. This concept has led to the design of three-dimensional structures such as the one shown in Fig. 13.1.^{[2][3]}

Interconnect. Three-dimensional structures require interconnections between the various levels. This is achieved by small, high aspect-ratio holes that provide electrical contact. These holes include the contact fills which connect the semiconductor silicon area of the device to the first-level metal, and the via holes which connect the first level metal to the second and subsequent metal levels (see Fig. 13.1). The interconnect presents a major fabrication challenge since these high-aspect holes, which may be as small as 0.25 μm across, must be completely filled with a diffusion barrier material (such as CVD titanium nitride) and a conductor metal such as CVD tungsten. The ability to fill the interconnects is a major factor in selecting a thin-film deposition process.

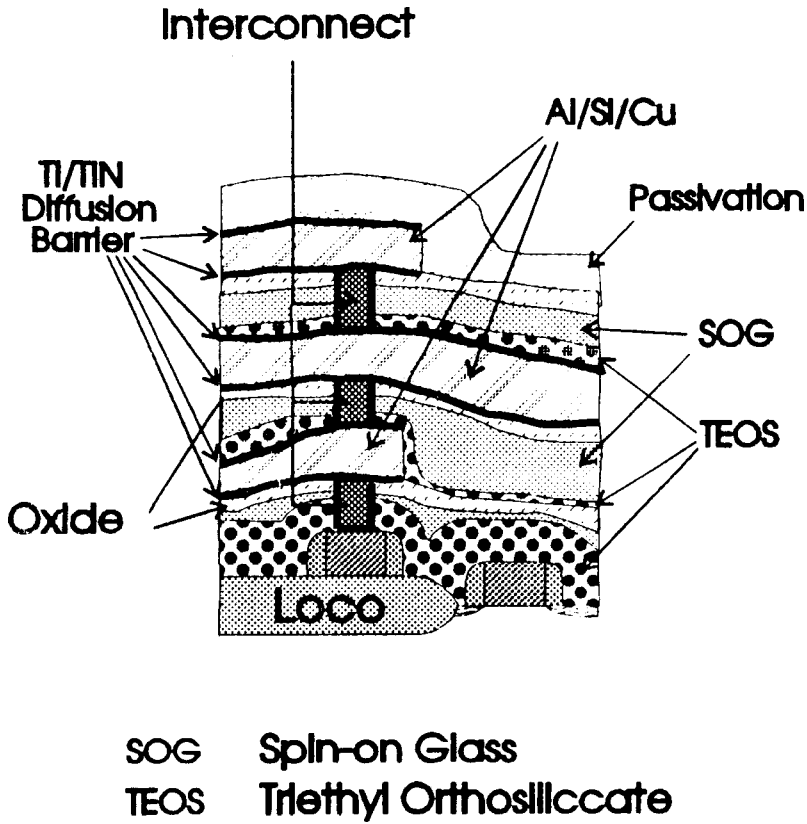


Figure 13.1. Cross-section of 0.5 μm triple-level integrated circuit (IC) with spin-on-glass planarization and Ti/TiN diffusion barrier.

2.5 Strained-Layer Superlattice (SLS)

Another concept for increasing device speed is the strained layer superlattice (SLS), which consists of alternating layers of semiconductor materials with thickness <10 nm deposited by CVD. These materials have the same crystal structure but different lattice

parameters. An example is an epitaxial layer of aluminum gallium arsenide ($\text{Al}_x\text{Ga}_{1-x}\text{As}$) deposited on a layer of gallium arsenide. These two materials have the same cubic crystal structure.

The strain resulting from the differences in lattice parameters is accommodated elastically, i.e., there is no dislocation in the films, providing that these differences are not too large. Only very thin layers can accommodate such strains. If the thickness is too great, the strain can no longer be absorbed elastically and a dislocation occurs (see Ch. 2, Fig. 2.11). The elastic strain alters the electronic band structure of the material, allowing conduction by light holes, thus greatly increasing the speed and reducing the power requirements.

2.6 Thermal Budget

An important consideration in the sequence of semiconductor devices fabrication is the so-called “thermal budget,” a measure of both the CVD temperature and the time at that temperature for any given CVD operation. As a rule, the thermal budget becomes lower the farther away a given step is from the original surface of the silicon wafer. This restriction is the result of the temperature limitations of the already deposited materials.

For instance, doped phosphosilicate glasses used in planarization cannot be heated above their flow temperature of 725°C . Likewise, after a layer of aluminum is deposited, subsequent temperatures cannot exceed 380°C because spiking and the formation of hillocks would occur rapidly (see diffusion barrier in the following chapter). The factor of *time at a given temperature* is just as important, as it will influence phenomena, such as diffusion and dissolution. In the planning of a CVD process, the sequence of events and the thermal budget are essential considerations.^[4]

3.0 CVD IN ELECTRONIC TECHNOLOGY

CVD is a major process in the production of thin films of all three categories of electronic materials: semiconductors, conductors, and insulators. In this chapter, the role of CVD in the fabrication of semiconductors is reviewed. The CVD production of insulators, conductors, and diffusion barriers is reviewed in the following chapter. The major semiconductor materials in production or development are silicon, germanium, III–V and II–VI compounds, silicon carbide, and diamond.

4.0 SILICON

4.1 Comparison of Properties

The electronic properties of silicon and other semiconductor materials are shown in Table 13.2.

The semiconductor properties of a material shown above can be summarized in two figures of merit shown in Table 13.3.

The Johnson figure of merit, based on saturated carrier velocity and dielectric strength (product of power \times frequency squared \times impedance), predicts the suitability of a material for high power applications. It is normalized with the value of one given to silicon. As shown in Table 13.2 below, diamond is clearly the preferred material on this basis.

The Keyes figure of merit, based on thermal conductivity as an additional factor, (see following section) predicts the suitability of a semiconductor for dense logic circuit applications. Again, diamond is far superior to other materials.

Table 13.2
Electronic Properties of Semiconductor Materials

Property	Si	GaAs	β SiC	CVD diamond
Dielectric constant (198 Hz)	11.8	10.9	9.7	5.5
Dielectric strength, Mv/cm	0.3–05	0.6	4.0	10
Bandgap (eV)	1.12	1.43	2.3–3.0	5.40
Saturated electron velocity (10^7 cm/s)	1.0	2.0	2.5	2.7
Carrier mobilities ($\text{cm}^2/\text{V}\cdot\text{s}$)				
electron (n)	1350–1500	8500	400–1000	2200
positive hole (p)	480	400	50	1000
Semiconductor temperature limit ($^{\circ}\text{C}$)	150	250	>1000	500
Thermal conductivity ($\text{W}/\text{cm}\cdot\text{K}$)	1.5	0.5	5	21

Although silicon cannot compete with other semiconductor materials in specific areas, it is overall an excellent material, a fact amply shown by its dominance of the market for the last forty years. It is readily available with a high degree of purity and relatively low cost. Most IC's are made from silicon and this is likely to remain so for some time.^[5]

CVD is used in silicon production in two major areas: 1) in the production of ultra-pure silicon from which single-crystal ingots are made, and 2) in the preparation of epitaxial and polycrystalline films.

Table 13.3
Figures of Merit for Semiconductor Materials

	Si	GaAs	InP	Diamond
Johnson figure of merit (high-power applications)	1	7	16	1138
Keyes figure of merit (dense logic circuits)	1	0.5	6	32

4.2 Single Crystal Processing

Silicon chips are fabricated by slicing a cylindrical ingot of single crystal silicon into thin wafers of up to 200 mm in diameter. Each wafer is then divided into approximately 100 chips. The performance of IC's depends to a great degree on the integrity and purity of these chips. Consequently the production of the single-crystal silicon ingot is most critical and requires very close control of impurities and fabrication process. CVD plays an important role in this process, since it is the basic method for preparation of electronic grade silicon (EGS). The single crystal ingot is obtained from the melted ESG by a crystal pulling operation^[5] (see Ch. 8).

4.3 Epitaxial Silicon

Epitaxy is a term that denotes the growth of a thin crystalline film on a crystalline substrate. When the epitaxial film is of the same material as the substrate (for instance silicon on silicon), the process is known as homoepitaxy. When film and substrate are of different

materials, it is heteroepitaxy (epitaxy is described in Ch. 2). CVD epitaxial-silicon films were developed originally to improve the performance of discrete bipolar transistors. They are now used extensively in field-effect transistors (FET), dynamic random access memory devices (RAM), and other IC designs. In short, epitaxial silicon films are an indispensable part of every microelectronic system.^{[6]–[9]}

The CVD reactions used to produce epitaxial silicon are described in Ch. 8. Originally, atmospheric-pressure CVD was used, but it is gradually being replaced by low-pressure CVD in spite of higher equipment cost and complexity. Low-pressure CVD appears to yield a better film with less autodoping and pattern shift.

To provide the necessary semiconductor properties, epitaxial films are normally doped by incorporating boron, arsenic, or phosphorus in the silicon structure by the addition of gases, such as the hydrides: arsine, diborane, and phosphine, during the deposition. Phosphorus as a dopant reduces internal stresses, increases the moisture resistance, and is used as an alkali getter (mostly of sodium). Boron as a dopant decreases the etch rate and improves step coverage.^{[10][11]} These elements are deposited from the hydrides as described in Ch. 3. Doping during CVD is gradually replacing doping by diffusion or by ion implantation.

4.4 Polysilicon

“Polysilicon” is a contraction of polycrystalline silicon, (in contrast with the single-crystal epitaxial silicon). Like epitaxial silicon, polysilicon is also used extensively in the fabrication of IC’s and is deposited by CVD.^[12] It is doped in the same manner as epitaxial silicon. Some applications of polysilicon films are:

- Gate electrodes in MOS devices for high value resistors to insure good ohmic contact to crystalline

silicon.

- Diffusion sources to form shallow junctions.
- Emitters in bipolar technology.

5.0 GERMANIUM

Although germanium was the original semiconductor material in early experiments and production, it is now rarely used as such but mostly as an alloy with silicon.^{[13]–[15]} Some applications of silicon/germanium are:

- Transistor with speed of over 60 GHz allowing as low as 1.5 V operation.
- Ge films on Si to tailor bandgap of heterostructures.
- Photovoltaic conversion and photodetectors.

6.0 III–V AND II–VI COMPOUNDS

6.1 General Characteristics

The III–V and II–VI compounds refer to combination of elements that have two, three, five, or six valence electrons. They have semiconductor properties and are all produced by CVD either experimentally or in production. The CVD of these materials is reviewed in Ch. 12. Many of their applications are found in optoelectronics where they are used instead of silicon, since they have excellent optical properties (see Ch. 15). Generally silicon is not a satisfactory optical material, since it emits and absorbs radiation mostly in the range of heat instead of light.

6.2 Gallium Arsenide

The most widely used of the III–V and II–VI materials is gallium arsenide, which is emerging as an important complement to silicon.^{[16][17]} Compared to silicon, it has the following advantages:

- Superior speed and power capability.
- Higher operating temperature.
- Capability of emitting light and ability to combine the processing of both photons and electrons on a single chip.
- Easily alloyed with other III–V compounds.
- High frequency capability (RF and MW).

For all its advantages, gallium arsenide has yet to be used on any large scale, at least outside optoelectronic applications. The reasons are cost (over ten times that of silicon), small wafer size, low thermal conductivity (1/3 that of silicon), and low strength.

Gallium arsenide is epitaxially deposited on a silicon substrate and the resulting composite combines the mechanical and thermal properties of silicon with the photonic capabilities and fast electronics of gallium arsenide.^{[11][18]}

6.3 Other Gallium Compounds

Other gallium-based III–V compounds are also produced by CVD, either experimentally or in production. The major ones are listed in Table 13.4.

Table 13.4
Optoelectronic Properties of Gallium Compounds

Material	E max. (eV)	Recombination process	Emission
GaAs _{1-x} P _x	2.0	Direct gap	Red
Ga _{1-x} Al _x As	1.9	Direct gap	Red
GaP	2.3	Indirect gap	Red, yellow, green
Ga _x In _{1-x} P	2.2	Direct gap	Yellow
Ga _{1-x} Al _x P	2.3	Pair emission	Green

The many possible combinations of II–V and II–VI compounds allow the tailoring of electronic and opto-electronic properties to suit specific applications. Of particular importance is the control of the stoichiometry of the element involved. This is achieved by the proper handling of the MOCVD reactions. Being able to tailor the bandgap imparts great flexibility in the design of transistors and optoelectronic devices.

The bandgap is defined as the energy difference between the top of the valence band of an atom and the bottom of the conduction band.^[19] The bandgap values of several semiconductor materials are shown in Fig. 2.12 of Ch. 2. The bandgap of GaAs is slightly greater than that of silicon, and that of AlAs is considerably greater. By alloying GaAs with Al to form Ga_xAl_{1-x}As or by partially substituting Al for Ga, a wide range of bandgaps can be produced as shown in Fig. 13.2.^[20] Indium can also be substituted for gallium, phosphorus for arsenic, and many other combinations are possible by the careful control of the CVD process.

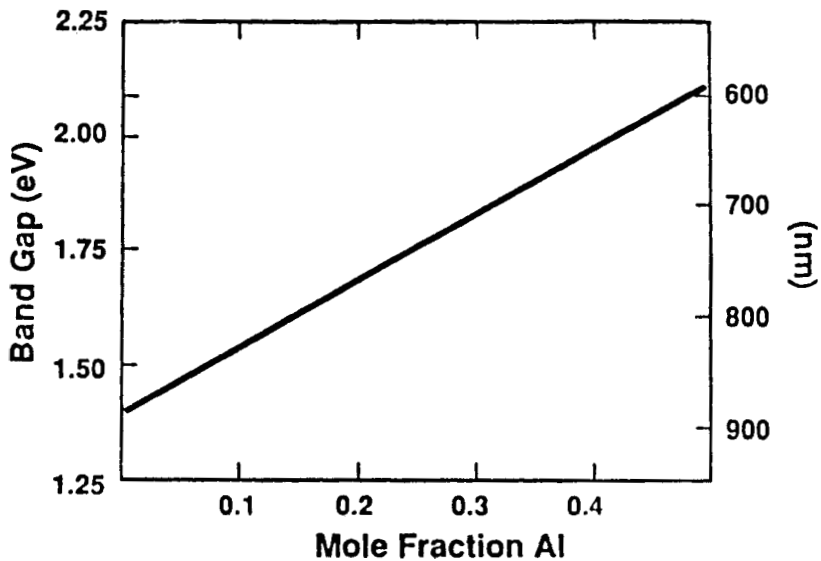


Figure 13.2. Bandgap of aluminum gallium arsenide as a function of composition at 300K.

Most of these compounds were originally prepared by liquid-phase epitaxy. That process is now largely replaced by MOCVD, particularly in the case of gallium arsenide, gallium arsenic phosphide, and gallium aluminum phosphide.

7.0 SILICON CARBIDE

7.1 General Characteristics

Silicon carbide occurs in two slightly different crystal structures: a single cubic form, βSiC , and a large number of hexagonal

rhombohedral varieties known collectively as α -SiC. β -SiC is an indirect-bandgap semiconductor with properties that promise significant improvements over existing semiconductor, such as silicon and gallium arsenide. This has long been recognized but it is only recently, with the development of high-quality single-crystal epitaxial thin film, that silicon carbide can be considered as a practical and useful semiconductor material.^{[21][22]} However, the development of SiC as a semiconductor is still mostly in the laboratory state, although considerable amount of work is being carried out in many laboratories.

7.2 Advantages of Silicon Carbide

The advantages of silicon carbide as a semiconductor material can be summarized as follows:

- It is intrinsically resistant to radiation.
- Its RF power output is more than an order of magnitude higher than similar III–V materials.
- Its high thermal conductivity and large bandgap allow operation of devices at high power and high temperature (600°C).
- It has a high saturation drift velocity, which enables devices to operate at higher frequencies.
- It has a high-temperature potential (>1000°C), which far surpasses that of other semiconductors.
- Its thin-film processing is compatible with silicon technology.

7.3 Thermal Stability

The bonding in silicon carbide is essentially covalent. These covalent bonds are strong since both atoms are small, the bond length

is short, and four of the six electrons of carbon and four of the fourteen electrons of silicon form bonds. The average bond energy is estimated at 300 KJ/mol. Because of this tight atomic structure, the high bonding strength and high melting point, silicon carbide has excellent thermal stability at temperature in excess of 600°C. Such a high-temperature potential far surpasses that of other semiconductors.

The high thermal stability of SiC also minimizes the solid-state diffusion problems which are prominent with silicon, although much work remains to be done in this area.

SiC should also be more effective than silicon or gallium arsenide particularly in microwave and millimeter-wave devices and in high-voltage power devices.

8.0 DIAMOND

8.1 General Characteristics

Another semiconductor material of great potential interest is CVD diamond, although the technology is still in the experimental stage (see Ch. 7). Pure single crystal diamond is one of the best electrical insulators. However, the presence of impurities can drastically alter its electronic state and, by suitable doping, diamond can be made into a remarkable semiconductor material. Diamond is normally an *indirect-bandgap, high-temperature* semiconductor, which can be changed from an intrinsic to an extrinsic semiconductor at room temperature by doping with other elements, such as boron or phosphorus.^{[23][24]} This doping is accomplished during deposition by introducing diborane (B_2H_6) or phosphine (PH_3) in the deposition chamber. The semiconductor properties of CVD diamond are similar to those of the single crystal.

8.2 Advantages of Semiconductor Diamond

As shown in Table 13.2, diamond has the widest bandgap of any semiconductor and an upper limiting semiconductor temperature lower than SiC but higher than other semiconductors. Diamond has a high electron carrier mobility exceeded in the p-type only by germanium and, in the n-type, only by gallium arsenide. The saturated carrier velocity, that is the velocity at which electrons move in high electric fields, is higher than for silicon, gallium arsenide, or silicon carbide. Unlike other semiconductors, semiconductor diamond retains its high saturated current velocity at high temperatures.

With such properties, it could be the ideal material for many semiconductor applications, such as high-power and high-frequency transistors and cold cathodes, or in the harsh environment found in internal-combustion and jet engines. With the advent of CVD diamond, it is now possible to take advantage of these properties.

8.3 Drawbacks of Diamond Semiconductor

Diamond, however, is not the universal semiconductor panacea: it is an *indirect bandgap* semiconductor and does not lase. In addition, present semiconductor materials, such as silicon and gallium arsenide, are solidly entrenched with a well-established technology, and competing with them will not be an easy task. CVD diamond will also compete with silicon carbide, which has also an excellent potential as a high-performance semiconductor material and is considerably easier and cheaper to produce.

Many problems must be solved before practical, reliable, and cost-effective diamond semiconductor devices become available. Yet, the prospects are good, particularly if epitaxial single-crystal or highly oriented polycrystalline diamond can be effectively produced by CVD.^[25]

8.4 Potential Applications

A number of semiconductor devices based on CVD diamond are being developed. One is a Schottky power diode capable of operating at 500°C, which has shown good rectification. Such a design would be ideal for high-voltage transistors with no need for voltage conversion from line to input. This would considerably reduce the size of the power supply. Another potential application consists of a series of field-effect transistors (MOSFET and MESFET), which are proving superior to silicon devices and are characterized by high power handling capacity, low saturation resistance, and excellent high frequency performance.

It is well recognized that CVD diamond would be the ideal material for many semiconductor applications, particularly in high power and high frequency systems such as microwave, as well as in harsh environments, such as in internal combustion and jet engines. However, many problems must be solved before practical, reliable, and cost-effective diamond semiconductor devices can be produced.^[25]

9.0 PROCESSING EQUIPMENT FOR CVD ELECTRONIC MATERIALS

Until about the 1970s, much of the CVD equipment for semiconductor applications was designed and built in-house and a CVD equipment industry was still embryonic. Since then, there has been a considerable shift to standardized systems built by specialized equipment manufacturers particularly for the semiconductor industry, and today sophisticated production and test equipment is readily available.

The Cluster Tool Concept. A recent trend in semiconductor equipment is the integration of two or more functions, such as CVD, PVD, etching, stripping, or rapid thermal processing, in one piece of equipment: the so-called *cluster tool*. A continuous vacuum can be maintained, a feature which reduces the handling and contamination problems, increases the overall throughput, improves the process control, and generally lowers the cost.

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14

CVD in Electronic Applications: Conductors, Insulators, and Diffusion Barriers

1.0 INTRODUCTION

CVD plays an increasingly important part in the design and processing of advanced electronic conductors and insulators as well as related structures, such as diffusion barriers and high thermal-conductivity substrates (heat-sinks). In these areas, materials such as titanium nitride, silicon nitride, silicon oxide, diamond, and aluminum nitride are of particular importance. These compounds are all produced by CVD.^{[1][2]}

2.0 THE CVD OF ELECTRICAL CONDUCTORS

2.1 Step Coverage and Conformity

The ability to coat a surface with a smooth film of constant thickness (conformity), and to fill a contact opening (interconnection)

evenly (step coverage) are major considerations when considering a given conductor material and the deposition process. New high-density IC designs may have over one million contact openings connecting the first layer of metal to the source/drain. Thin spots at the bottom of the interconnection and overhang at the top (keyhole) must be avoided as shown in Fig. 14.1.

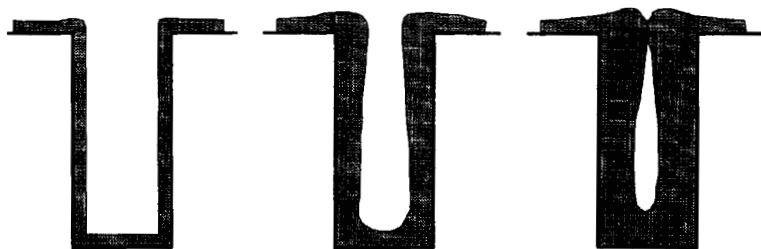


Figure 14.1. Keyhole formation in non-conformal coatings.

The interconnecting holes are narrow and deep (at times less than $0.25\text{ }\mu\text{m}$ wide and up to $2\text{ }\mu\text{m}$ or more in depth) and, after a diffusion-barrier layer is applied, it must be filled completely with a high-conductivity metal (usually aluminum or tungsten) to provide the low-resistance plug for inter-layer connections. Typically, CVD provides better step coverage and conformity than sputtering and other physical-vapor deposition processes.

A typical example of the complexity of interconnection assembly consists of a MOCVD-TiN diffusion barrier combined with a low-temperature (260°C) CVD aluminum with low resistivity ($<3\text{ }\mu\Omega\text{-cm}$). A copper doping forms an overlying sputtered Al-Cu film. This aluminum plug provides a large reduction in resistance compared to the classical tungsten process.^{[3][4]}

2.2 Aluminum and Electromigration

Aluminum has long been the metal of choice for electrical conductors in semiconductor devices. It is readily evaporated and can be processed by CVD at low temperature (see Ch. 6). However, it has a major drawback, which is its tendency to electromigrate, i.e., the gradual displacement of metal from one part of the line to another when an electrical current is applied. This results in the formation of spikes that penetrate the silicon junction and cause electrical shorting. This phenomenon occurs with high current density (greater than 10^6 amp/cm²), which is often used in new circuit designs. Once electromigration is started, it can only intensify. This propensity to form spikes and the ready diffusion of silicon into the aluminum are a fundamental weakness of the aluminum-silicon couple.

To mitigate the problem, a diffusion barrier is incorporated between the aluminum and the silicon (see Sec. 5 below). It is also possible to replace aluminum by alloys of aluminum and copper or aluminum and silicon, which have less tendency to electromigration. These alloys are usually deposited by bias sputtering. However, they offer only a temporary solution as electromigration will still occur as greater densities of circuit elements are introduced. It was recently determined that improvements in the deposition of aluminum by MOCVD at low temperature with a dimethyl aluminum hydride precursor may reduce the problem.^[1]

The electromigration problem has led to the investigation of other electrical-conductor materials, such as tungsten (presently used in contact and via fills) and more recently copper.

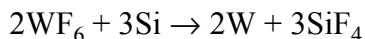
2.3 Refractory Metals

Tungsten has good electromigration resistance and relatively low resistivity (5–6 $\mu\text{ohm-cm}$). Originally applied by sputtering, it is now produced mostly by CVD, generally using the hydrogen reduction of tungsten hexafluoride (see Ch. 6). A cold-wall reactor is normally used with lamp heating of the substrate.

Tungsten for Interconnections. CVD tungsten is now replacing sputtered aluminum for the filling of interconnection holes with the following advantages:^{[5][6]}

- Deposition can be selective or non-selective.
- No patterning is necessary for selective deposition.
- Non-selective films are easily patternable by wet or dry etching technology.
- Blanket deposition has excellent conformal coverage.
- Films can be deposited over a wide range of temperature.
- Electromigration is far less than that of aluminum.
- A good barrier to Al-Si interaction is provided up to 450°C for 30 min.
- Films have low stress on Si and other substrates.
- Films have low contact resistance, especially if a silicide layer is deposited between W and Si.

Certain problems remain to be solved before tungsten can be adopted on a large scale for metallization, such as the erosion of silicon during deposition, which occurs according to the following reaction:



This reaction proceeds at a much faster rate than the hydrogen reduction of WF_6 . The result is erosion of the silicon substrate causing encroachment and tunnel defects. The use of a different precursor, such as tungsten carbonyl, $\text{W}(\text{CO})_6$, may solve this problem. CVD tungsten is presently limited mostly to multilevel-via-fill applications.

Molybdenum. Molybdenum is another refractory metal with low resistivity (5–7 $\mu\text{ohm-cm}$) now under investigation for metallization of IC's. It is usually deposited by the decomposition of the carbonyl, $\text{Mo}(\text{CO})_6$, or by the hydrogen reduction of the halide (MoCl_5 or MoF_6). These reactions are described in Ch. 6.

2.4 Copper

Copper is intrinsically a better metal than aluminum for the metallization of IC's. Latest developments in MOCVD show that it can be readily deposited without major changes in existing processing equipment. Diffusion problems are minimized and it appears that present barrier materials, such as titanium nitride or titanium-tungsten alloys, should provide adequate diffusion barriers for the copper-silicon couple, certainly up to the highest temperatures presently used in IC's processing (see Ch. 6). The development of CVD copper for semiconductor metallization is on a considerable scale at this time.^{[7][8]}

Researchers in Japan have determined that copper interconnects deposited by metallo-organic chemical vapor deposition (MOCVD), then followed by chemical mechanical polishing, provides sub-quarter-micron interconnects and can be achieved on a production basis. Titanium nitride and borophosphosilicate glass provide effective barriers against copper diffusion.^{[9]–[11]}

CVD copper is competing directly with sputtering which, at this stage, is still the preferred production process. The semiconductor industry is shifting massively from aluminum to copper for chip metallization.

2.5 Silicides

Considerable work is in progress in the development of silicide materials for electronic applications. These compounds are used increasingly as conductive thin films and are replacing

metals in a number of applications. They are also replacing polycrystalline silicon conductors in VLSI's because of their low resistivity (1/10 that of silicon), their much higher thermal stability and their excellent diffusion barrier characteristics.^[2] CVD is a major process in the production of silicides (see Ch. 12).

Of particular interest are the refractory metal silicides, such as MoSi_2 , TiSi_2 , WSi_2 , TaSi_2 , and CoSi_2 , which are especially suitable for gate metallization, and the silicides of the platinum group metals, which are suitable for making contacts.

The most widely used at the present time are WSi_2 and TaSi_2 . WSi_2 is deposited almost exclusively by low-pressure CVD. On the other hand, films of CVD TaSi_2 suffer from undesirable growth morphology and further research is needed. TaSi_2 is mostly deposited by sputtering.

The "salicide" concept (self-aligned silicide) is now used extensively in MOSFET devices. It is based on TiSi_2 and CoSi_2 , both of which are deposited by CVD.^{[12][13]} The CVD reactions for the deposition of silicides are described in Ch. 12.

The silicide and salicide technologies are particularly important in Japan and may indicate a general switch to these materials whenever appropriate.^[14] In one case, epitaxial cobalt disilicide provided a satisfactory diffusion source and is mentioned as a promising alternative for deep submicron devices.^[15]

2.6 Trends in Metallization

The trend in CVD metallization is toward greater use of copper, and the refractory metals and their silicides in multilayered metallization designs, typically consisting of metal-silicide contacts, refractory-metal barriers, and copper or an aluminum alloy as the principal interconnect metal. Other metals deposited by CVD such as chromium, molybdenum, platinum, rhodium, and ruthenium are also actively considered for use as conductors.

3.0 THE CVD OF ELECTRICAL INSULATORS (DIELECTRICS)

Thin films of electrical insulators are essential elements in the design and fabrication of electronic components. The most widely used insulator materials (dielectrics) are silicon oxide (SiO_2) and silicon nitride (Si_3N_4). These materials are extensively produced by CVD.

3.1 Silicon Dioxide (SiO_2)

The uses of CVD silicon dioxide films are numerous and include insulation between conductive layers, diffusion masks, and ion-implantation masks for the diffusion of doped oxides, passivation against abrasion, scratches, and the penetration of impurities and moisture. Indeed, SiO_2 has been called the pivotal material of IC's.^[6] Several CVD reactions are presently used in the production of SiO_2 films, each having somewhat different characteristics. These reactions are described in Ch. 11.

Some of the most significant developments in the CVD of SiO_2 include experiments in plasma CVD at 350°C via electron cyclotron resonance (ECR) to gain improved control of the deposition rate and obtain a quality equivalent to that of the thermally grown oxide (see Ch. 5). Deposition from diacetoxyditertiarybutoxy silane at 450°C has also been shown to significantly improve the SiO_2 film properties.^[4]

Another important recent advance is the development of the CVD of SiO_2 from tetraethylorthosilicate (TEOS) and ozone (see Ch. 11). This deposition reaction is becoming prominent for the many production advantages it provides.^{[16]–[19]}

A recent competitor to CVD in the planarization of silicon dioxide is the sol-gel process, where tetraethylorthosilicate is used to form spin-on-glass (SOG) films (see Appendix). This technique produces films with good dielectric properties and resistance to cracking. Gas-phase precipitation, which sometimes is a problem with CVD, is eliminated.

3.2 Silicon Nitride

Silicon nitride (Si_3N_4) is an excellent electrical insulator, which is increasingly replacing SiO_2 because it is a more effective diffusion barrier, especially for sodium and water which are major sources of corrosion and instability in microelectronic devices.^[20] As a result, it can perform two functions simultaneously: passivation and provision of a diffusion barrier. It is now used in the fabrication of integrated circuits in such areas as oxide insulation masking (to be removed during subsequent processing), local oxidation of silicon (known as LOCO), and as a dielectric between two layers of polysilicon for capacitors in analog cells. It is generally deposited by plasma CVD or by sputtering.

4.0 THE CVD OF SUBSTRATES (HEAT SINKS)

4.1 The Need for Heat Dissipation

The design of integrated circuits (ICs) has reached the point where one million or more components can be put on a single chip (known as very large scale integration or VLSI) and higher densities will soon be needed as circuit designers are constantly demanding higher performance, expanded memory, faster access time, and shrinking geometry.

The increase in density of IC's, especially in microwave, millimeter-wave, and opto-electronic devices such as laser diodes and laser-repeater assemblies, is presently limited by the large amount of heat generated by the extremely close packing of the electronic components on the chip and the high frequencies and power levels. Likewise, new laser diodes have extremely high intensity of light output, which is further increased when the diodes are placed in arrays. Here again, the limiting factor in the performance of such devices is the ability to dissipate the heat in the package.

To remove this unwanted heat (also known as thermal management), it is often necessary to use hybrid circuits and bulky heat-dissipation devices or complicated and expensive refrigeration. Metals with good thermal conductivity, such as copper or aluminum, are presently used as heat sink materials but, since being metals they also have high electrical conductivity, they require an electrical-insulation barrier.

4.2 Heat-Sink Materials

Heat dissipation can be effectively dealt with by using substrate materials such as aluminum nitride, beryllia and, more recently, diamond which combine electrical insulation with high thermal conductivity. The relevant properties of these three materials are shown in Table 14.1.

Beryllia (BeO) is an excellent heat-sink material which is presently widely used but is being phased out because it presents acute safety problems.^[21] It is being replaced by aluminum nitride which extensively produced by CVD, mostly in Japan (see Ch. 10, Sec. 2).^[22]

4.3 Diamond Heat-Sinks

Diamond is an electrical insulator with the highest thermal conductivity at room temperature of any material and compares favorably with beryllia and aluminum nitride.^{[23]–[25]} It is undoubtedly the optimum heat-sink material and should allow clock speeds greater than 100 GHz compared to the current speed of less than 40 GHz.

Heat sinks, in the form of thin slices prepared from single-crystal natural diamond, are already used commercially but are limited in size to approximately 3 x 3 x 1 mm. These single-crystal diamonds are gradually being replaced by CVD diamond, which is now available in shapes up to 15 cm in diameter.^{[26]–[28]} The high cost of CVD diamond may remain a factor for many years and CVD aluminum nitride should remain the material of choice at this time.

Table 14.1
Properties of Heat-Sink Materials

Properties	CVD		
	AlN	BeO	Diamond
Resistivity, ohm•cm	10^{14}	10^{14}	10^{12} – 10^{16}
Dielectric constant @ 1 MHz	8.8	6.7	5.6
Dielectric strength, kV/mm	10^5	10^5	10^6
Thermal conductivity, W/m•K	140–220	260	1700
Specific heat, J/g•K	0.7	1.0	0.51
Thermal expansion (0–400°C), $10^{-6}/^{\circ}\text{C}$	4.1	7.2	2.0

5.0 THE CVD OF DIFFUSION BARRIERS

5.1 Principle of Diffusion Barriers

The geometry of modern semiconductor devices is continuously shrinking and will soon reach the 0.20 μm bench mark, with great increase in speed and efficiency. To accomplish this goal requires major advances in materials and fabrication processes. Many obstacles remain and one of the most critical is that of solid-state diffusion and the development of diffusion barriers.^{[1][20]}

Diffusion is a physical phenomenon, which occurs when the atoms of a solid move into another solid above a certain temperature. Diffusion is particularly pronounced with silicon into aluminum, as mentioned in Sec. 2.2 above. It occurs during subsequent processing steps when the temperature exceeds 400°C.

To prevent or reduce diffusion, a barrier is placed between the two materials. The ideal barrier material must not react with the materials it separates and have suitable electrical and thermal properties. Many designs call for the barrier to be deposited with constant thickness inside very narrow ($0.35\text{ }\mu\text{m}$) and deep holes (aspect ratio of 2 to 1 or more).

5.2 Diffusion Barrier Materials

Three major barrier materials are now in use and all three are deposited either by CVD or by sputtering.^[29]

- Titanium is used as a *sacrificial* barrier, that is, it is gradually consumed during the heating process. It is deposited by CVD or sputtering (see Ch. 6).
- Titanium-tungsten is an intermetallic, composed mostly of tungsten. It is an excellent barrier if it is “stuffed,” that is, with nitrogen added into the crystalline defects. It prevents diffusion of silicon into aluminum up to 500°C . It is deposited mostly by sputtering.
- Titanium nitride is a truly *inert* ceramic barrier, which is effective to 550°C . It is deposited by MOCVD or sputtering (see Ch. 10).

In devices with geometry below the $0.25\text{ }\mu\text{m}$ level, titanium nitride will likely replace titanium-tungsten, since it has better barrier properties. The process of choice will likely be CVD, which offers improved uniformity and step coverage, although improvements in collimated sputtering may keep that process on line for a while.

Tantalum Nitride as Diffusion Barrier. Tantalum nitride (TaN) produced by MOCVD has excellent potential as a barrier material, comparable to TiN. The resistivity of TaN thin films can be lowered by rapid thermal annealing in nitrogen.^[30]

Ternary Nitrides as Diffusion Barriers. Barrier layers with good step coverage and low resistivity are formed from ternary nitrides with various compositions: Ti-Si-N, W-Si-N, and W-B-N. They are deposited by MOCVD with deposition temperatures between 300 and 450°C. Complete step coverage is obtained on reentrant features as low as 0.25 micron with an aspect ratio of 4.0.^[31]

5.3 Example of Diffusion Barrier

A typical semiconductor device (found in the back-end of the line or the interconnects) consists of a layer of glass followed by a sputtered layer of titanium, which is thermally treated to form a titanium silicide. Next, a layer of titanium nitride is deposited on top of the silicide and on the sidewall of the contacts by sputtering or by MOCVD (see Fig. 13.3 in Ch. 13).^{[20][32]} This layer of TiN acts as a diffusion barrier and an adhesion promoter. It is followed by the main interconnect, which is an aluminum-copper alloy, in turn followed by another layer of TiN, which acts as adhesion and antireflecting layer.

6.0 THE CVD OF SUPERCONDUCTORS

The discovery of high-temperature superconductivity in mixed oxides, such as the lanthanum-barium-copper oxide complexes, has created a great deal of interest in these materials. Superconductivity, that is, the absence of any resistance to the flow of electric current, is now possible at temperatures above the temperature of liquid nitrogen (77K). Many problems remain in the development of practical processes for these materials and commercialization is not likely to occur until these problems are solved. Among the several processing techniques now used, CVD appears one of the most successful.^{[33]–[36]}

Table 14.2 lists the principal copper-oxide complexes now under development and their properties. The CVD reactions used to deposit these materials are described in Ch. 11.

The most likely CVD applications of these superconductors to reach the practical stage are coatings for semiconductor and other electronic-related applications. For larger current-carrying applications, a superconductor coating over a metallic conductor such as copper may also become a practical design because of its advantage over a monolithic superconductor wire. It is able to handle current excursions and has better mechanical properties.

The metal alloy, niobium germanium (Nb_3Ge), is another superconductor with a much lower transition temperature (20K) with well-established characteristics and good strength. It is deposited by CVD on an experimental basis by the reaction described in Ch. 6.

Table 14.2
Properties of Superconducting Materials

Compound	Transition temperature K	Current capacity A/cm^2
$\text{YBa}_2\text{Cu}_3\text{O}_7$	93	10000
$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$	110	2000
$\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_x$	125	1000

Applications of CVD superconductors now being considered include the following:

- Josephson junctions for passive microwave devices, satellite-communication systems, and computer logic gates.
- Magnetic field detectors (superconducting quantum interference devices or SQUIDS).
- Magnet wires of $\text{YBa}_2\text{Cu}_3\text{O}_7$ for motor generator and energy storage systems.
- Superconducting short dipole antenna materials with a resonant frequency of 550 MHz.

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CVD in Optoelectronic and Ferroelectric Applications

1.0 CVD IN OPTOELECTRONICS

Optoelectronics is a discipline which combines optics and electronics. It deals with optical wavelengths from 0.20 μm (ultra-violet) to 3 μm (near infrared) as shown in Fig. 15.1. The properties of optoelectronic materials are a useful combination of electrical and semiconductor properties (electron action), with optical properties such as transmission, reflection, and absorption (phonon action).

Optoelectronics is a relatively new and fast-growing industry with many applications. Thin-film processes, such as reactive sputtering, molecular-beam epitaxy (MBE), and particularly MOCVD, play a major part in their production. Equipment and materials are similar to those used in the semiconductor industry and many companies manufacture both types of products. In fact the distinction between the two areas is often blurred. Statistics generally do not single out optoelectronics as such and, for that reason, it is difficult to define the scope of the industry accurately.

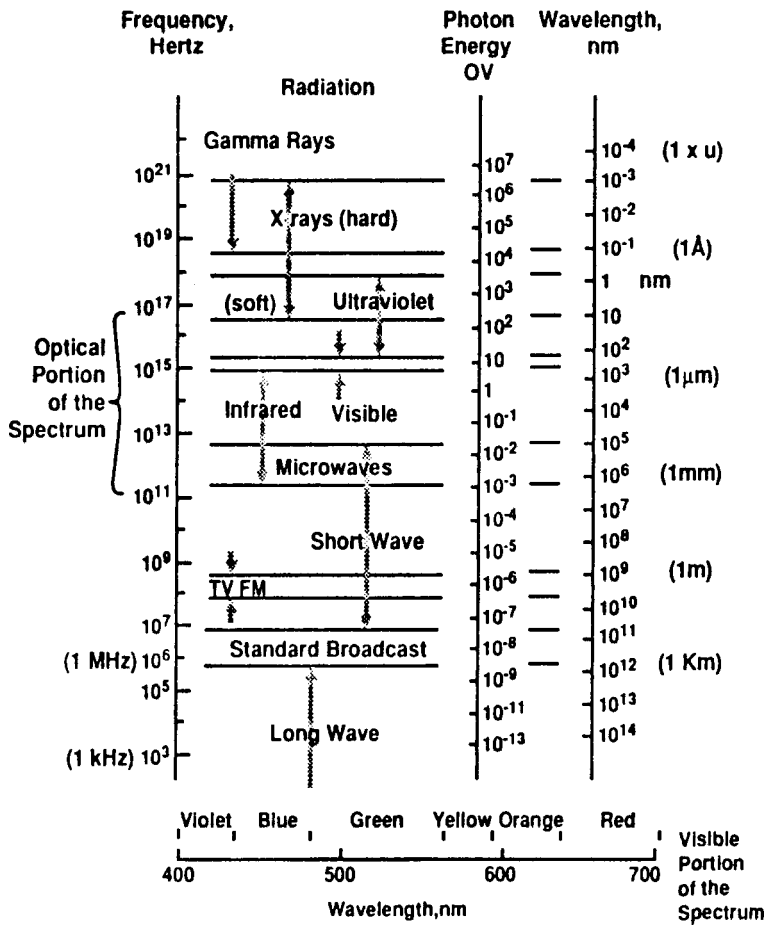


Figure 15.1. Electromagnetic spectrum.

2.0 OPTOELECTRONIC MATERIALS

2.1 Critical Properties

The critical properties for optoelectronic materials are bandgap (operating range), carrier lifetime (efficiency), and resistivity (response time). To optimize these properties, it is necessary to have control of the process parameters such as:

- Stoichiometry (bandgap definition).
- Carrier concentration and mobility (resistivity).
- Defect density (carrier lifetime).

2.2 Silicon

Silicon is not as prominent a material in optoelectronics as it is in purely electronic applications, since its optical properties are limited. Yet it finds use as a photodetector with a response time in the nanosecond range and a spectral response band from 0.4 to 1.1 μm , which matches the 0.905 μm photoemission line of gallium arsenide. Silicon is transparent beyond 1.1 μm and experiments have shown that a red light can be produced by shining an unfocused green laser beam on a specially prepared ultrathin crystal-silicon slice.^[1] CVD may prove useful in preparing such a material.

2.3 III–V and II–VI Compounds

The III–V and II–VI semiconductor compounds have excellent optical properties and are the most important group of optoelectronic materials, which are all produced by CVD for many optoelectronic applications. The properties of these materials and their CVD reactions are reviewed in Ch. 12, Secs. 3.0 and 4.0 and Ch. 13, Sec. 6.0. It is possible to tailor the bandgap, by the proper combination of these materials, to suit any given application (See Fig. 13.2 of Ch. 13).

Among the wide variety of possible combinations, the most common are the III–V compounds of gallium, such as gallium arsenide, gallium arsenic phosphide, gallium aluminum arsenide, gallium phosphide, gallium indium phosphide, gallium indium arsenide, and gallium aluminum phosphide. Other common compounds are indium arsenide (InAs), indium phosphide (InP), boron phosphide (BP), indium arsenide antimonide (InAsSb), aluminum arsenide (AlAs), and others.

Commonly used II–VI compounds include zinc sulfide, zinc selenide, zinc telluride, cadmium sulfide, cadmium telluride, and mercury cadmium telluride. These materials are not as widely used as the III–V compounds, one reason being that it is difficult to achieve p-type doping. Mercury cadmium telluride is used extensively in military night sights, which detect in the 8–13 μm spectral band (a similar material, platinum silicide, is being developed for that purpose). The major applications of CVD II–VI compounds are found in photovoltaic and electroluminescent displays.

3.0 OPTOELECTRONIC CVD APPLICATIONS

Optoelectronic devices are found in numerous consumer products such as television, compact-disk players, laser communications, laser printers, radar detectors, cellular telephones, direct-broadcast television, and many others. Many of these applications were developed in Japan and that country is still prominent in the field.

Optoelectronic components produced by CVD include semiconductor lasers, light-emitting diodes (LED), photodetectors, photovoltaic cells, imaging tubes, laser diodes, optical waveguides, Impact diodes, Gunn diodes, mixer diodes, varactors, photocathodes, and HEMT (high electron mobility transistor). Major applications are listed in Table 15.1.^[4]

Some of the most important optoelectronic devices are described below.

Table 15.1
Optoelectronic Devices and Applications

Device	Applications
Photodiode (LED)	Cameras, strobes, illuminators, remote controls, IR sensors
Pin photodiode	Fiber-optic communications, fiber links
Laser detector	Digital audio disks, video disks, laser-beam position sensors, distance sensors
Photodiode array (LED)	Photodiode chips can be arrayed monolithically or non-monolithically to any element
Photo transmitters	Optical switches, strobes, toys
IR-emitting diodes (GaAs)	Remote controls, optical switches, optoisolators, choppers, pattern recognition devices
IR-emitting diodes (GaAlAs)	Optical switches, encoders, photo IC sensors
Photo interrupter	Highly precise position sensors, non-contact switches
Reflective sensor	Tape-end sensors, liquid-level sensors
Optic receiver	Optic remote controllers
Photocoupler	Isolators, impedance converters, noise suppressors

3.1 Light Emitting Diodes (LED)

Light emitters, such as the carbon arc or the incandescent lamp, are well-known but those of interest here are the light-emitting diode (LED) and the laser. In a light-emitting diode of appropriate semiconductor material, light is emitted when electrons are made to flow across the p-n junction (Fig. 15.2). Electrons must be energized with a certain voltage in order to cross the p-n junction. After crossing, they return to their normal state and, in so doing, produce light in a very narrow wavelength.

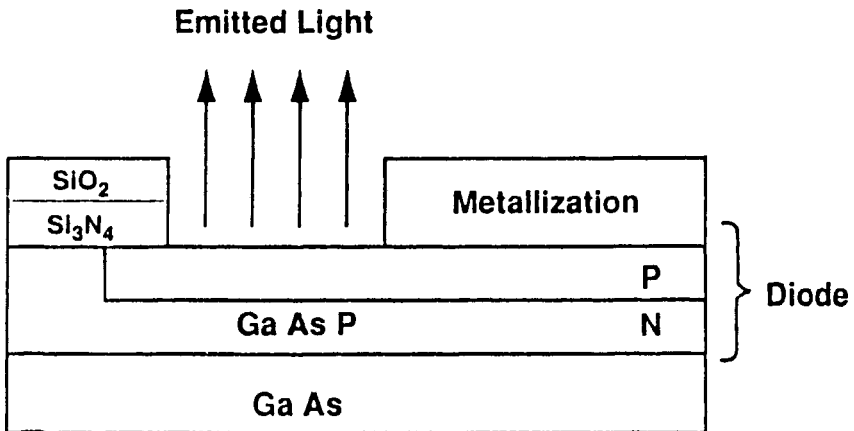


Figure 15.2. Schematic of typical light-emitting diode (LED).

A variety of colors, such as green, amber, and red (and infrared), can be obtained with different semiconductor materials without the need for a filter (see Ch. 13, Table 13.4). A LED (or photodiode) device may consist of multiple diodes in an array operating in the reverse-bias mode. Patterns of light showing symbols, letters, or numbers can thus be produced with different colors obtained by doping the semiconductor material by CVD or ion implantation.

LED materials include gallium arsenic phosphide, gallium aluminum arsenide, gallium phosphide, gallium indium phosphide, and gallium aluminum phosphide. The preferred deposition process is MOCVD, which permits very exacting control of the epitaxial growth and purity. Typical applications of LED's are watches, clocks, scales, calculators, computers, optical transmission devices, and many others.

3.2 Light Detectors

Light detectors fall into two categories: photoconductors and photodetectors. Photoconductors are devices whose resistance decreases upon exposure to light. Cadmium sulfide (CdS) and cadmium selenide (CdSe) are the most commonly used photoconductor materials in the visible spectrum. They are still mostly produced by sputtering but CVD is used increasingly (see Ch. 12, Sec. 4.0).

Photodetectors operate by carrier transport across a semiconductor junction. A wide variety of these photodiodes are available, such as Schottky diodes, phototransistors, and avalanche photodetectors. Typical photodetector materials are gallium arsenic phosphide and gallium phosphide, which are produced by MOCVD or MBE.

3.3 Semiconductor Lasers

The light produced by a laser has a much more narrow wavelength than the light of an LED or other light sources (Fig. 15.3). In addition, laser light is coherent, i.e., the photons travel in parallel paths from the source. Lasers made of thin-films are similar to bulk lasers (He-Ne, ruby) except that they are more compact and efficient. Due to the short lifetime of the photons, high-frequency modulations are possible.

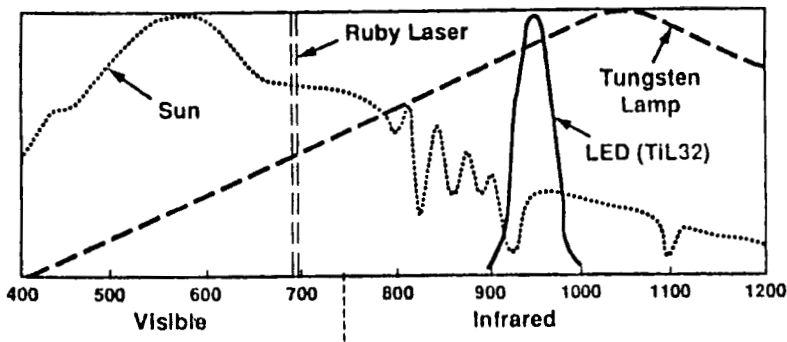


Figure 15.3. Radiation wavelengths of the sun, an LED, a ruby laser, and a tungsten lamp.

The design of semiconductor lasers is similar to that of LED's and consists of a p-n junction between two different direct bandgap semiconductors with light-emitting capability. Many semiconductor materials are suitable but the most common are $\text{Al}_x\text{Ga}_{1-x}\text{As}_y\text{Sb}_{1-y}$ and $\text{Ga}_x\text{In}_x\text{As}_y\text{P}_{1-y}$. Some of these new laser designs are based on the quantum-well principle, in which a very thin layer of a semiconductor with a high bandgap, such as gallium aluminum arsenide, is sandwiched between two films of gallium arsenide, which has a smaller bandgap. This design can increase by tenfold the

amount of generated light over that emitted by a standard semiconductor laser.

Since only a low current is required, it is possible to build an array of such lasers on a single chip. This may lead the way to optical logic circuits for computers. A similar design uses active layers of gallium indium arsenic phosphide, 60 nm thick, sandwiched between indium-phosphide buried layers for integrated digital networks. Another design is comprised of four alternate layers of indium gallium arsenide and indium gallium arsenic phosphide, each 6 to 7 nm thick, which are deposited on a diffraction lattice substrate for lasers. These materials are all produced by MOCVD.^{[5][6]}

3.4 MOCVD and MBE

MOCVD and MBE (molecular-beam epitaxy) are presently the two major processes for the production of optoelectronic thin films, which are capable of meeting the extremely stringent property requirements of the new designs (the MBE process is described in the Appendix). Both MOCVD and MBE produce high-quality materials with similar purity, mobility, and photoluminescence properties, but MOCVD is more suitable for large-scale production since MBE requires extremely low pressure and has low deposition rates. In addition, MOCVD is better for phosphorous compounds, for aluminum gallium arsenide, and for alloys with two Group V elements (As, Sb, Bi). It also seems to produce better heterojunction bipolar transistor structures.^[7] On the other hand, MBE has two major advantages: better film-growth control and more abrupt interfaces.

The two processes are becoming closer in concept. For instance, MOCVD is using techniques developed for MBE such as in situ characterization monitoring, load lock, and lower pressure levels, and MBE is now using chemical sources such as organometallics, which are typical of CVD.

4.0 CVD IN PHOTOVOLTAIC

A photovoltaic material generates a voltage when it is exposed to light and photovoltaic can be considered as a specialized area of optoelectronics. The principle has been known for many decades but it became a industrial reality only in 1958 when an array of photovoltaic cells, based on single-crystal silicon, provided power for a space vehicle.

4.1 Photovoltaic Principle and Operation

A photovoltaic cell is basically a semiconductor diode consisting of a junction similar to the junction of a transistor. An electrical potential is formed by n-type doping on one side and p-type on the other. Under the impact of light (photons), such as in sunlight, electrons move from the p side, across the junction to the n side, and, through electrical contacts, can be drawn as a usable current (Fig. 15.4).

A major limitation of photovoltaic cells is their low efficiency. Sunlight consists of photons with a large range of frequencies, and consequently, an equally large range of energies. However, a given photovoltaic material responds only to the photons which have sufficient energy to lift an electron from the valence band to the conductive band across the bandgap. Photons with insufficient energy merely pass through without any effect or with detrimental heating of the cell. The most efficient photovoltaic materials are those that respond to the widest possible range of photon frequency, such as amorphous silicon, gallium arsenide, and other III–V compounds.

The thickness of a photovoltaic cell is chosen on the basis of its ability to absorb sunlight, which in turn depends on the bandgap and absorption coefficient of the semiconductor. For instance, 5 nm of crystalline silicon are required to absorb the same amount of sunlight as 0.1 nm of amorphous silicon and 0.01 nm of copper-indium diselenide. Only MBE and MOCVD are capable of producing such extremely thin films.^[8]

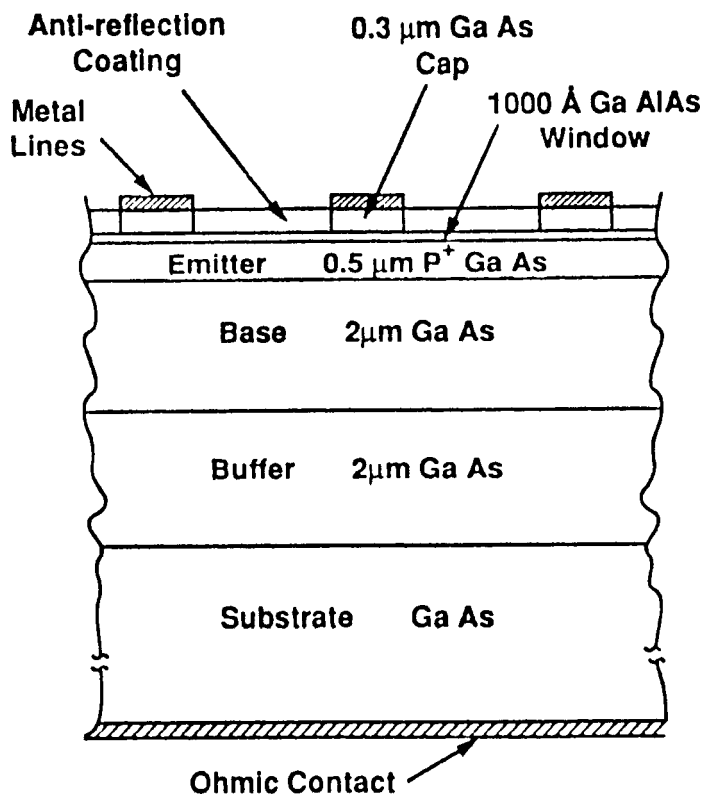


Figure 15.4. Typical photovoltaic (solar) cell.

4.2 Photovoltaic Materials and Processing

Many materials with photovoltaic capability are known but only the following have been developed for commercial applications.

Single-Crystal Silicon. Silicon is still the dominant material in photovoltaic. It has good efficiency, which is 25% in theory and 15% in actual practice. Silicon photovoltaic devices are made from wafers sliced from single crystal silicon ingots, produced in part by CVD (see Ch. 8, Sec. 5.1). However, silicon wafers are still costly, their size is limited, and they cannot be sliced to thicknesses less than 150 μm . One crystalline silicon wafer yields only one solar cell, which has an output of only one watt. This means that such cells will always be expensive and can only be used where their high efficiency is essential and cost is not a major factor such as in a spacecraft applications.

Amorphous Silicon (a-Si). Amorphous silicon is considered a promising new material.^{[9]–[11]} As mentioned above, only a very thin coating is necessary, since the amorphous structure is much better at absorbing sunlight than is the crystalline material. The most common process to produce a-Si is the decomposition of silane by plasma CVD (see Ch. 8).^[12] Thicknesses of a few micrometers can be deposited and, in contrast with single crystal silicon, relatively large areas can be covered. The drawbacks of α -Si are:

- Deposition is still slow and quality needs to be improved.
- Cost must be reduced considerably before solar cells of amorphous silicon could be considered for large-scale power generation.
- Efficiency is still low and a-Si lacks stability, as it degrades and loses efficiency when first exposed to sunlight (Staebler-Wronski effect). However, the efficiency stabilizes in time.

A thin film of tin oxide with a rough texture, produced by MOCVD from tetramethyl tin, $(\text{CH}_3)_4\text{Sn}$, deposited on an amorphous silicon cell provides a light-trapping surface, which enhances the efficiency of the device.^[13]

Deposition has been carried out on architectural glass yielding single-junction amorphous silicon with an efficiency of 13% in the laboratory, but with lower efficiency in production devices. An atmospheric-pressure deposition system is shown in Fig. 15.5. The gas injection device is shown in Fig. 15.6.

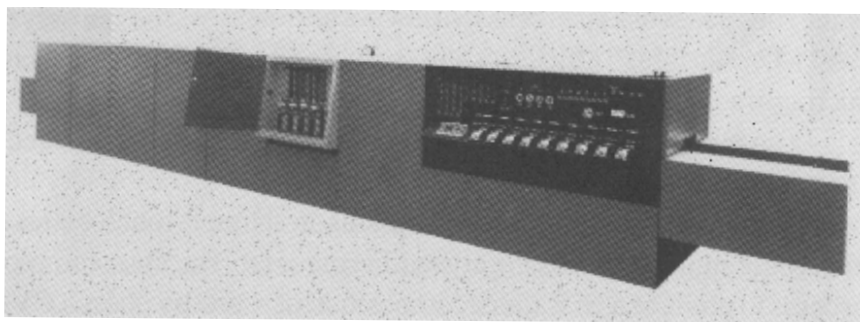


Figure 15.5. Atmospheric-pressure CVD production system for the deposition of photovoltaic coating. (Source: Watkins-Johnson, Palo Alto, CA)

Other Photovoltaic Materials. Several other photovoltaic materials are being actively developed. A promising system uses a multijunction in which several layers of optoelectronic materials are tailored to respond to specific wavelengths, thus converting a greater proportion of the light spectrum to electricity. An example incorporates an upper layer of indium phosphide (InP), which absorbs the visible part of the light spectrum and a second layer of indium gallium arsenide (InGaAs), which absorbs the infrared portion.^[14]

Cells made of CVD epitaxial gallium arsenide and its alloys have shown the highest efficiency (over 22% recorded against a theoretical value of 39%). However, cost is high. Other materials are being investigated, such as copper indium selenide (CuInSe_2), cadmium telluride (CdTe) with an efficiency of 14.6%, indium phosphide (InP), which has high resistance to radiation, the sulfides, selenides, and tellurides of lead, selenium, germanium, and the combination zinc

telluride/cadmium telluride/gallium arsenide (ZnTe,CdTe,GaAs). These materials are all deposited by MOCVD.^{[15]–[17]}

Transparent semiconductor oxide films, such as tin oxide (SnO_2) and zinc oxide (ZnO), produced by MOCVD are also being considered for photovoltaic applications.^[18]

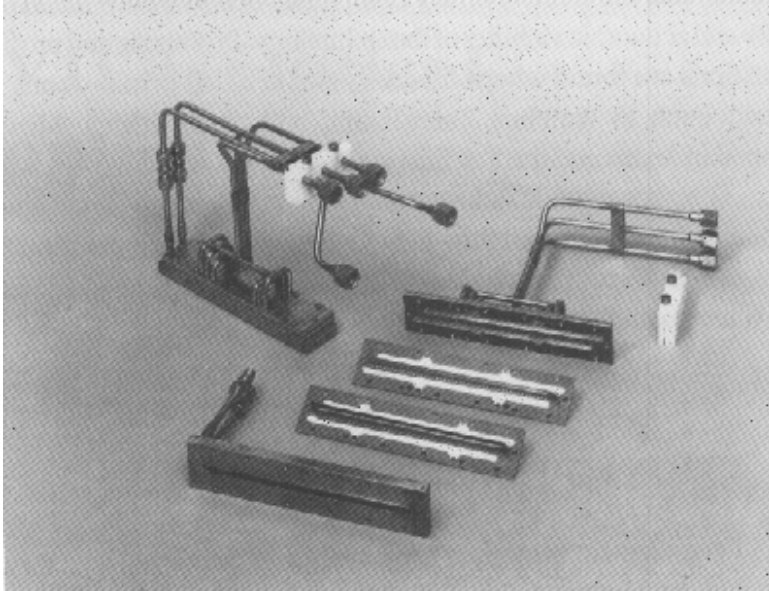


Figure 15.6. Detail of gas injector system for atmospheric CVD of photovoltaic materials. (Source: Watkins-Johnson, Palo Alto, CA)

4.3 Photovoltaic Applications

Originally photovoltaic devices were restricted to space applications, due to their high cost. In the last few years, cost has been reduced by more than an order of magnitude and the spectrum of applications is now much broader.

Besides space-power generation, the most publicized applications are in experimental grid-power plants intended for eventual competition with classical power sources for large-scale generation of electricity. The market for grid power is still small and essentially experimental but may see a large expansion if any of the planned demonstration plants are successful and the electric utility companies become convinced of the validity and economic viability of the technology. Promising and profitable applications are found when solar cells are included in many consumer products such as watches, calculators, and many others. Most are produced in Japan and the Far East at this time.

The photovoltaic industry is slowly expanding with continuous advances in materials and thin-film technology. The deposition techniques, which were at first based mostly on sputtering and evaporation, are now increasingly relying on CVD.

5.0 CVD IN FERROELECTRICITY

Ferroelectric materials are capable of being polarized in the presence of an electric field. They may exhibit considerable anomalies in one or more of their physical properties, including piezoelectric and pyroelectric coefficients, dielectric constant, and optoelectronic constant. In the latter case, the transmission of light through the material is affected by the electric field, which produces changes in refractive index and optical absorption coefficient. Varying the applied field changes the phase modulation.^[19]

Important ferroelectric materials are those with piezoelectric characteristics. They are crystalline ceramics that exhibit expansion along one crystal axis and contraction along another when subjected to an electrical field. Conversely, compression generates an electrical voltage across the material. These materials have a large number of industrial applications.

Bulk ferroelectric materials are produced from powder by standard ceramic processing techniques but thin-film processing is becoming increasingly preferred. The deposition processes were, until recently, mostly RF reactive sputtering, reactive ion plating, reactive MBE, and solgel. CVD, particularly MOCVD, is now being used increasingly either experimentally or in production as the technology improves and new precursor materials become more readily available.

CVD-derived powders may prove very useful and profitable in the production of bulk ferroelectric materials which are produced by hot-pressing or sintering. These powders offer great uniformity, small particle size, and high reactivity (see Ch. 19).

5.1 CVD Ferroelectric Materials

Ferroelectric compounds made by CVD include the following mixed oxides (see Ch. 11, Sec. 11.0) for the CVD reactions).^{[20]–[22]}

- Lead titanate (PbTiO_3) with excellent pyroelectric and piezoelectric properties.
- PZT (lead zirconate titanate) and PLZT (lead lanthanum zirconate titanate). Powder of these materials produced by CVD are being investigated.
- Strontium titanate, SrTiO_3 , with a high dielectric constant (310 for single crystal) and high refractive index.^[23]
- Bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, with a high dielectric constant and a high dielectric strength.^[24]
- Lithium niobate, LiNbO_5 .^[25]

Other ferroelectric CVD materials include:

- Cadmium sulfide (see Ch. 12).
- Aluminum nitride with a large piezoelectric coupling factor and a high surface acoustic wave velocity (5650 m/sec) (see Ch. 10).
- Zinc oxide with high surface acoustic wave velocity (see Ch. 11).

5.2 Applications of Ferroelectric CVD Materials

The major piezoelectric applications are sensors (pickups, keyboards, microphones, etc.), electromechanical transducers (actuators, vibrators, etc.), signal devices, and surface acoustic wave devices (resonators, traps, filters, etc.). Typical materials are: ZnO, AlN, PbTiO₃, LiTaO₃, and Pb(Zr.Ti)O₃ (PZT).

The major pyroelectric applications are those related to infrared sensing such as cooking controls, fire or heat alarms, door openers, etc. Typical materials are: LiTaO₃, PbTiO₃, and Pb(Zr.Ti)O₃.

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16

CVD in Optical Applications

1.0 INTRODUCTION

The science and technology of optics are rapidly advancing, spurred by the development of the laser and optical storage. Until recently, optical coatings were produced mostly by evaporation, usually for single-layer antireflection applications or for superimposed layers of high and low refractive index materials for spectrally selective filters. The laser required far more complex systems and prompted a considerable development of thin-film materials and technology. These films are now playing a major role in most optical applications.

Evaporation, the original coating process, is relatively low cost and simple to apply. However, evaporative coatings generally show a pronounced columnar structure, which causes much light scattering, a high wavelength shift with temperature and time, and a high stress. For these reasons, evaporation is gradually being replaced by other thin-film processes, primarily standard and ion-beam sputtering and, more recently, solgel. CVD techniques, such as plasma CVD and MOCVD, are also strong contenders, especially in high-quality applications or where surfaces of three-dimensional objects are to be coated.

2.0 OPTICAL CHARACTERISTICS

Thin films are used to modify the optical characteristics of a system and a brief review of these characteristics is in order.

The Electromagnetic Spectrum. The optical properties of a material are related to the electromagnetic spectrum (see Ch. 15, Fig. 15.1). The portions of the spectrum of interest are the following:

- The visible, that is the range of wavelength that can be detected and identified as colors by the eye, extending from 0.4 to 0.7 μm .
- The infrared (IR) of wavelength immediately above the visible ranging from 0.7 to 3 μm (for present optical applications). IR radiation is a major source of heat.
- The ultraviolet (UV) with a range of wavelength immediately below the visible (from 0.19 to 0.4 μm for optical applications).

Reflectance. The optical property of reflectance is the ratio of reflected flux of light to the incident flux. Unless otherwise specified, the total reflectance is meant, which includes specular and diffuse reflectance.

Transmittance. Transmittance is the ratio of the radiant flux transmitted by a material to the incident flux.

Absorption. Absorption, the attenuation of a beam through a transparent medium, can be characterized by an absorption coefficient. For thin films, such as those of optical oxides, absorption is very small and can usually be ignored. In metallic or semiconductor coatings however, absorption is a major factor.

Index of Refraction. The index of refraction is the ratio of the velocity of light in air to the velocity of light in the material at a given wavelength. When light (including IR and UV radiations) travels in a

transparent medium, such as air, and meets another medium, such as glass, a division of the light energy occurs, part being transmitted through the glass and part reflected. These optical effects are illustrated in Fig. 16.1.

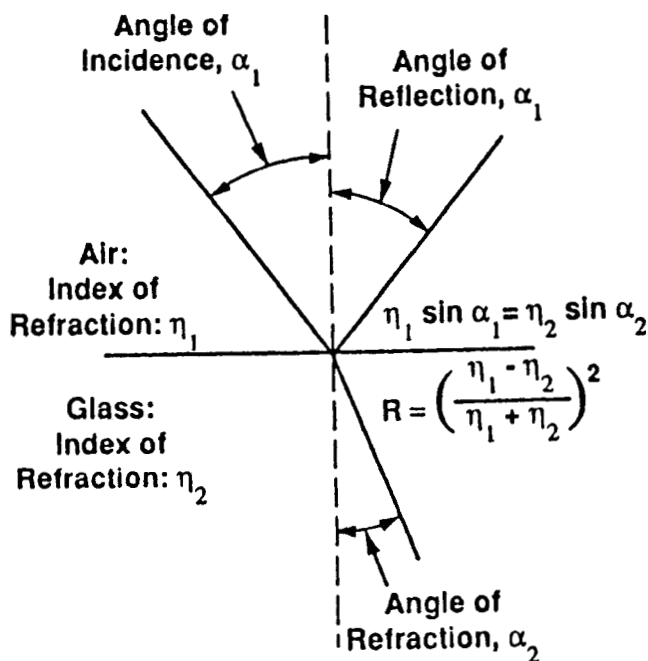


Figure 16.1. Diagram of light reflection and refraction.

3.0 OPTICAL MATERIALS PRODUCED BY CVD

Most inorganic optical coatings are oxides, such as TiO_2 , SiO_2 , and ZrO_2 , or nitrides, such as Si_3N_4 and BN. Thin films of metals, such as aluminum, silver, or gold, are also used for reflecting unwanted heat or where electrical conductivity is a requirement.

The following is a partial list of optical materials which are presently obtained by CVD either in production or experimentally:

- SnO_2 for emissivity control (low-E glass).
- Multilayers of oxides with high refractive index (TiO_2 , ZrO_2 , HfO_2 , ThO_2) and low refractive index (SiO_2) for antireflection coatings.
- SiO for filters (2.7 μm band).
- SnO_2 and indium tin oxide (ITO) for conductive transparent coatings on glass for electromagnetic interference (EMI) applications.
- Fe_2O_3 for beam splitters and interference layers.
- Ta_2O_3 as antireflective coatings and hot mirrors.
- Amorphous silicon for photothermal conversion.
- Nitrides of Ti, Zr, and Hf for optical selectivity.^[1]
- Molybdenum thin films for IR reflectance.^[2]
- Tungsten thin films from $\text{W}(\text{CO})_6$ for reflectivity control.^[3]
- Nitrides by plasma CVD as antireflection coatings for photovoltaic cells.^[4]
- Alternating layers of Si_3N_4 and SiO_2 for color filters.^[5]

4.0 OPTICAL APPLICATIONS OF CVD

4.1 Antireflection Coatings

The function of an antireflection (AR) coating is to reduce the surface reflection of optical elements and increase the amount of light transmitted. The glare and ghost images from secondary reflections are minimized. Multiple coatings are now produced that can

reduce the reflection to 0.3% or less over a broad band of frequencies. A typical AR material is magnesium fluoride, MgF_2 .

Most AR coatings are still produced by evaporation but CVD is gradually introduced particularly in applications with three-dimensional surfaces or deep recesses. AR coatings are used in numerous applications, which include lasers, lenses for cameras and binoculars, instrument panels, microscopes, telescopes, range finders, etc., as well as on automotive and architectural glasses.

4.2 Reflective Coatings

The purpose of a reflective coating is to provide maximum reflectivity. The major application is found in mirrors. In addition to reflection, other properties, such as abrasion resistance and good adhesion to glass, are often required. A common reflective material is aluminum, which has excellent reflectivity. However, it has poor abrasion resistance and adhesion. Because of that, it is being replaced in many critical applications by metals such as chromium, rhodium, molybdenum, or tungsten, which have much better abrasion resistance and improved adhesion, although their reflectivity is not as high. These metals are deposited by sputtering and to a lesser degree by CVD.

Reflective coatings are found in astronomical instruments, telescopes, spectrometers, range finders, projectors, microfilm readers, television tubes, diffraction gratings, interferometers, beam splitters, lasers, and many other applications.

4.3 Heat and Light Separation Coatings

Heat- and light-separation coatings (also known as hot and cold mirrors) are important applications that separate the hot (infrared) from the cold (visible) radiation. The principle is shown schematically in Fig. 16.2. The transmittance of a cold mirror is shown in Fig. 16.3a. This mirror is coated with a dielectric film reflecting more than 90% of the

visible spectrum while transmitting more than 80% of the IR (below 8000 μm). The hot mirror uses the opposite principle by reflecting the IR and transmitting the visible (Fig. 16.3b). Tin oxide and indium tin oxide (ITO) are excellent IR reflectors and are both deposited by CVD (see Ch. 11).

Hot- and cold-mirror CVD coatings are used in projectors to maintain the film gate at low temperature and avoid damaging the film. They are also used increasingly in tungsten-halogen lamps.^[6]

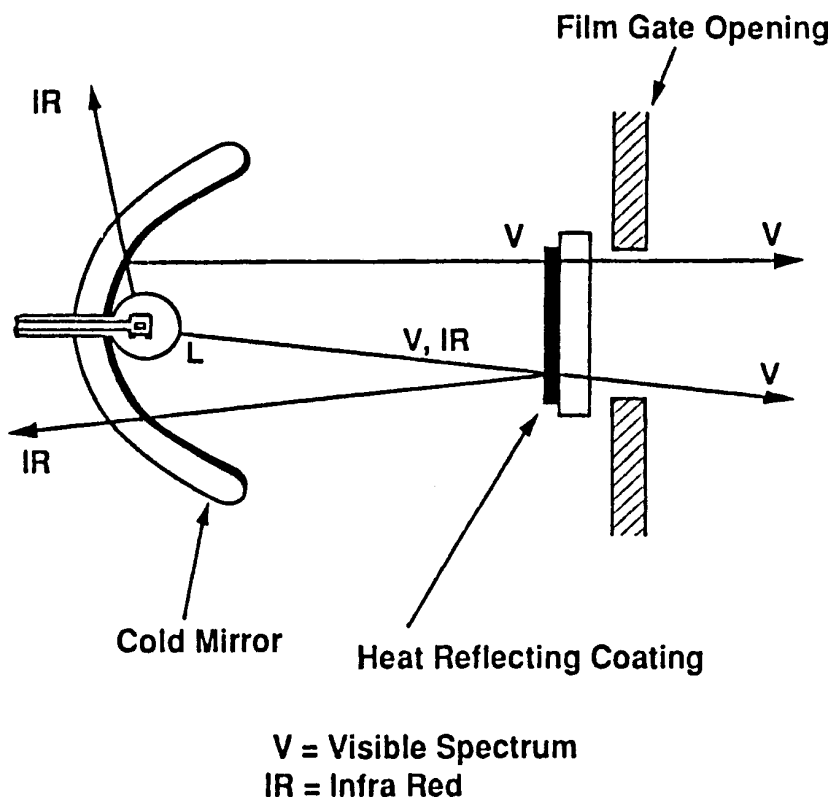
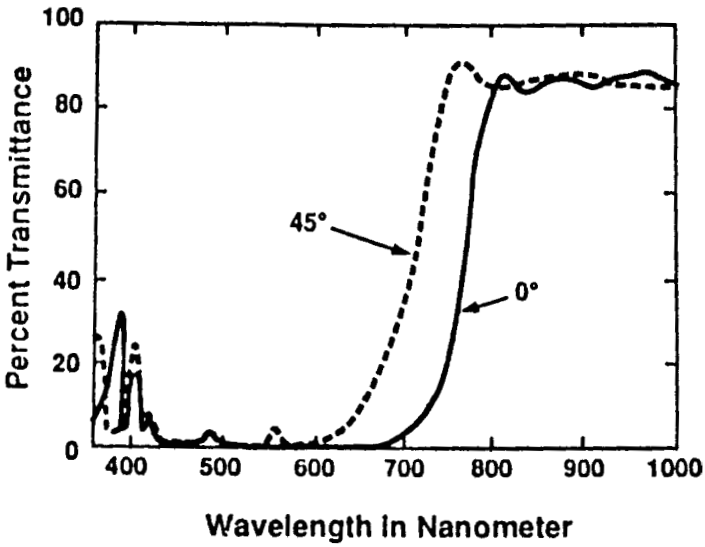
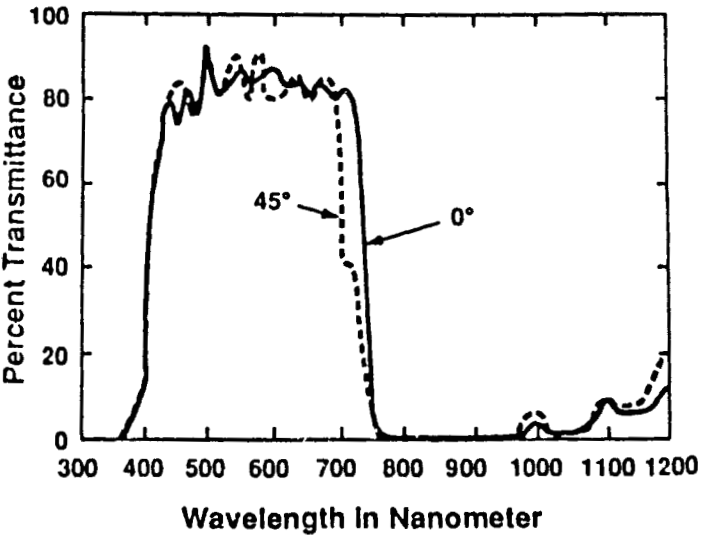


Figure 16.2. Diagram of operation of hot and cold mirrors.



(a)



(b)

Figure 16.3. Reflection and transmittance of hot and cold mirrors.

4.4 Electrically Conductive Transparent Coatings

Some metal oxides have the unique property of being electrically conductive, in contrast with the majority of oxides, which are good dielectrics at least at room temperature. The most widely used conductive oxides are tin oxide (SnO_2) and indium oxide (In_2O_3). The latter is usually doped with tin oxide (90% indium, 10% tin) and is known as ITO (indium tin oxide). In the form of thin films on glass, these oxides have good reproducible electrical conductivity and high light transmission in the visible spectrum. In addition, ITO films are stable and have good resistance to abrasion. They can be acid etched to specific line geometry by standard photoresist techniques. Their properties are shown in Table 16.1.

Table 16.1
Properties of Transparent Electrically Conductive Coatings

	Noble Metals	Tin Oxide	ITO
Thickness (nm)	7–35	10–300	10–300
Surface resistivity (Ω per square)	1–30	80–50000	7.5–1000
Luminous transmission %	70–85	70–80	75–90
Abrasion resistance	Good	Excellent	Very good
Chemical resistance	Excellent	Excellent	Very good
Flatness	Conforms to substrate	Distorts substrate	Conforms to substrate
Adhesion	Excellent	Excellent	Excellent
Resistivity stability	Excellent	Very good	Good
Cost	Moderate	Low	Moderate

These coatings are used to prevent the transmission of radio frequency interference from sources such as television or computer displays, as antistatic coatings, and to absorb or reflect microwaves.

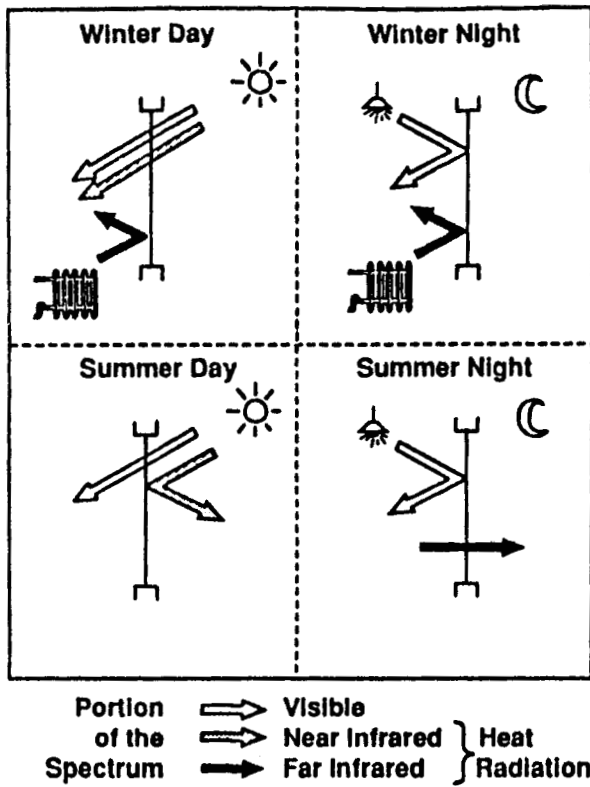
Windshield De-Icing: A potentially important application of electrically conductive films is in deicing automobile and aircraft windshields. The coating comprises a low-resistance thin metallic layer sandwiched between two antireflection oxide layers and especially designed bus bars to distribute the electrical energy evenly. To provide erosion resistance, the coating is sandwiched within the safety glass. A 3 mm (1/8 in.) layer of ice can be removed in 2 min. at -13°C . Also under development are reflective and low-emissivity coatings for all automobile glass areas to reduce the heating and cooling load.

Sputtering is presently the major thin-film process for the production of deicing coatings. The coating is satisfactory from an optical standpoint although transmission could still be improved, but it has poor scratch resistance and must be sandwiched between the two layers of safety glass. The CVD oxides films shown in Table 16.1 are particularly attractive since they are inherently abrasion resistant and could be used on the outer surface of the glass.

4.5 Architectural-Glass Coating

A major application of thin films is the coating of glass to control the effects of solar radiation in buildings. Ideally, such films should regulate the transmission and reflection of the solar spectrum as shown in Fig. 16.4. The solar heat energy wavelengths are limited to the near infrared (up to $2\text{ }\mu\text{m}$) while the average heat energy from a heated room is mostly in the far infrared. As a result, a coating system should have controllable optical properties so that, in the winter, it would have a high transparency for the visible and the near infrared part of the spectrum and a high reflectivity for the far infrared.

Conversely, in the summer, it would still have a high transparency for the visible, but a high reflectivity for the near infrared and a high emissivity for the far infrared. The present state of the art of thin-films deposition still falls short of this goal which may have to wait for the development of suitable photochromic coating materials.



Winter characteristics of coating:

- Transparent to visible and near IR
- Reflective to far IR

Summer characteristics of coating:

- Transparent to visible
- Reflective to near IR
- High emissivity to far IR

Figure 16.4. Ideal characteristics of optical coatings for architectural glass.

Present coatings (known as low-E coatings) allow sufficient light inside and reflect a controlled amount, particularly in the infrared spectrum, thereby reducing cooling loads (Fig. 16.5). In the US, two-thin film processes are presently used to deposit these coatings: sputtering and CVD (solgel coating is also used mainly in Germany). The development of large and efficient sputtering systems now allows the production of coatings with good adhesion and closely controlled thickness (in the nm range), which is essential to maintain a uniform level of absorption.

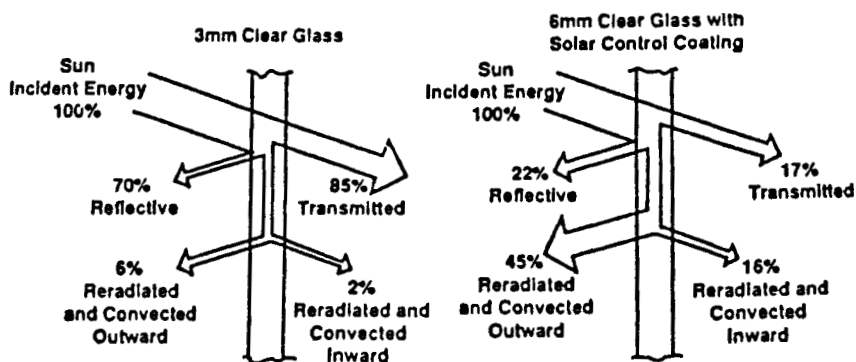


Figure 16.5. Performance of present architectural-glass coatings.

CVD, the other major deposition process, is used on a large scale. A typical low-E glass is obtained by depositing a thin film of silicon dioxide followed by another thin film of fluorine-doped tin oxide. The SiO_2 acts as a diffusion barrier and the SnO_2 reduces the emissivity. A typical CVD apparatus is shown in Fig. 16.6.^{[8]–[10]} These films are deposited at atmospheric pressure on the hot glass in a continuous operation (float-glass process). The CVD reactions are described in Ch. 11.

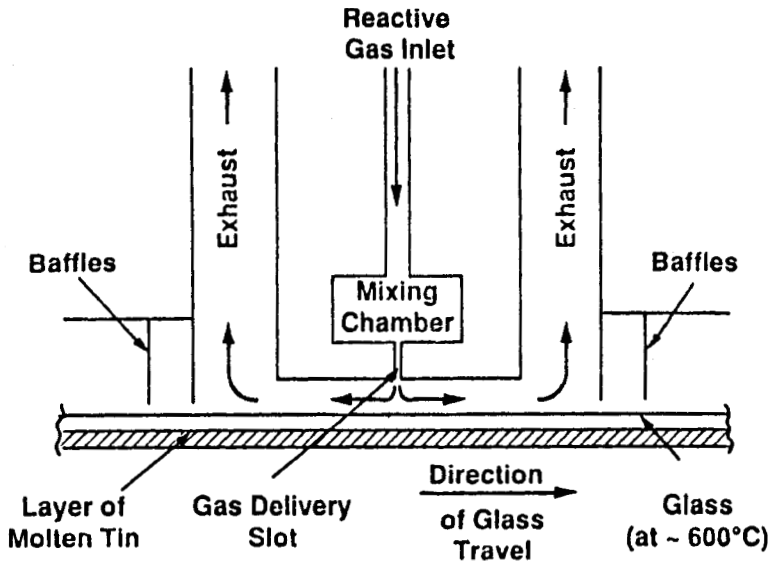


Figure 16.6. Diagram of CVD apparatus for the deposition of solar-control coatings on glass.

4.6 Infrared Optics

Infrared optics is a fast growing area in which CVD plays a major role, particularly in the manufacture of optical IR windows.^[11] The earth's atmosphere absorbs much of the infrared radiation but possesses three important bandpasses (wavelengths where the transmission is high) at 1–3 μm , 3–5 μm and 8–17 μm . As shown in Table 16.2, only three materials can transmit in all these three bandpasses: single crystal diamond, germanium, and zinc selenide.

Single-crystal diamond is the ideal material with remarkable optical properties, high heat resistance, extreme hardness, and excellent chemical resistance. But, because of its high cost and size limitation, it is only used in exceptional cases, such as the window

for the Pioneer Venus spacecraft. The development of CVD production techniques may eventually allow its use on a large scale (see Ch. 7).

Table 16.2
Properties of Infrared Window Materials

Material	Useful Transmission Range (wavelengths in μm)
Single-crystal diamond	1–3, 3–7.5, 8–17
Diamond-like carbon	7–6
Silicon	1–3, 3–5
Germanium	1–3, 3–5, 8–17
Barium fluoride, BaF_2	1–3, 3–5, 8–12
Zinc sulfide, ZnS	1–3, 3–5, 8–10
Zinc selenide, ZnSe	1–3, 3–5, 8–17

The most common IR window materials are zinc sulfide, which is translucent, and zinc selenide, which is transparent. Both of these materials are made by low-pressure CVD by the reaction of vaporized zinc and hydrogen sulfide or selenide (see Ch. 12). Germanium, another common IR window material, is also produced by CVD (see Ch. 8).

These materials have the ability to transmit IR radiation with a minimum of absorption. They also have a high refractive index that does not vary to any extent with temperature or wavelength and are the chosen materials in applications where it is essential to minimize lens curvature and thickness. However, a high refractive index causes high reflectivity, as much as 36% for a germanium surface. The use of an anti-reflective (AR) coating is then necessary in order to increase the amount of light transmitted, reduce glare and ghost reflections, and obtain a clearer image.

Diamond-like carbon (DLC) provides excellent AR coatings with an adjustable index of refraction, which varies with the hydrogen content and can be tuned to fit a given optical design. DLC coatings are particularly well suited for germanium windows, with 90% average transmission in the 8 to 12 μm wavelength, as shown in Fig. 16.7, and to zinc sulfide windows, where they provide a reflectance value of 0.7% average in the 8 to 12 μm range. Adhesion to the zinc sulfide can be optimized by using an intermediate film of germanium.^[10] DLC coatings are deposited by CVD as described in Ch. 7.

4.7 Trends in CVD Optical Applications

The following is a listing of recent optical applications, either present or potential, where CVD may play a major role.

- *Coatings for gas-discharge light bulbs.* Gradually replacing incandescent bulbs, these bulbs are more efficient, but require a coating to reflect the IR radiation back into the filament.
- *Coatings for optical storage.* Most of these coatings are processed by sputtering or evaporation but MOCVD is being actively considered.
- *Ultraviolet coatings for excimer lasers.* These lasers are likely to play a large role in lithography of very high density computer chips.^[13]
- *Bidiffractive grating coupler with CVD TiO_2 film.*^[14]

The major optical coating process remains evaporation. However, sputtering, solgel, and CVD are making inroads because of the better properties they provide.^[15] At this time, it is not clear which coating process will prove best but CVD, because of the excellent bond and hardness of the deposited materials and the relatively moderate cost of the equipment, is a good candidate.

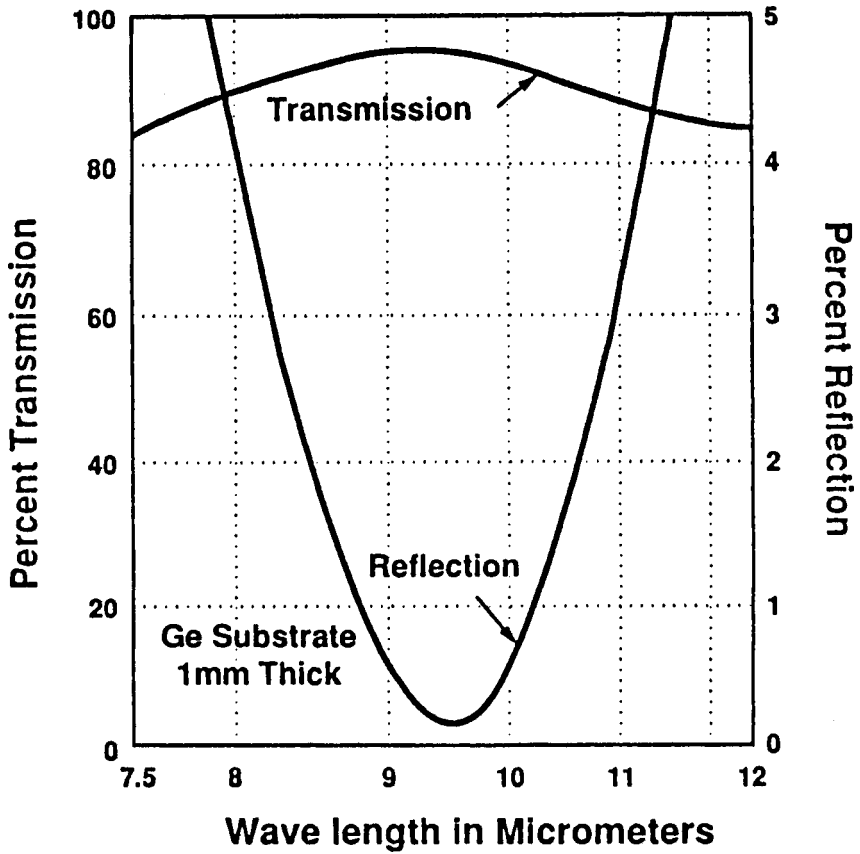


Figure 16.7. Transmission and reflection of germanium coated with diamond-like carbon (DLC).

5.0 CVD IN OPTICAL-FIBER PROCESSING

5.1 Optical Considerations

Optical communications have a large capacity for the transmission of information and, in this respect, is far superior to

communication by electrical signals.^[16] A typical system uses optical fibers as waveguides and a source of light, such as a light-emitting diode (LED) or a laser in either the visible or the infrared spectrum. These fibers consist of a glass core, which transmits the light, and a SiO₂ cladding with a lower index of refraction to keep the light within the fiber. The lower index of refraction is obtained by the addition of dopants, such as boron oxide (B₂O₃) or germanium dioxide (GeO₂), to silica during the deposition.

Three basic types of optical fibers are produced by CVD (Fig. 16.8) as described below.^[17]

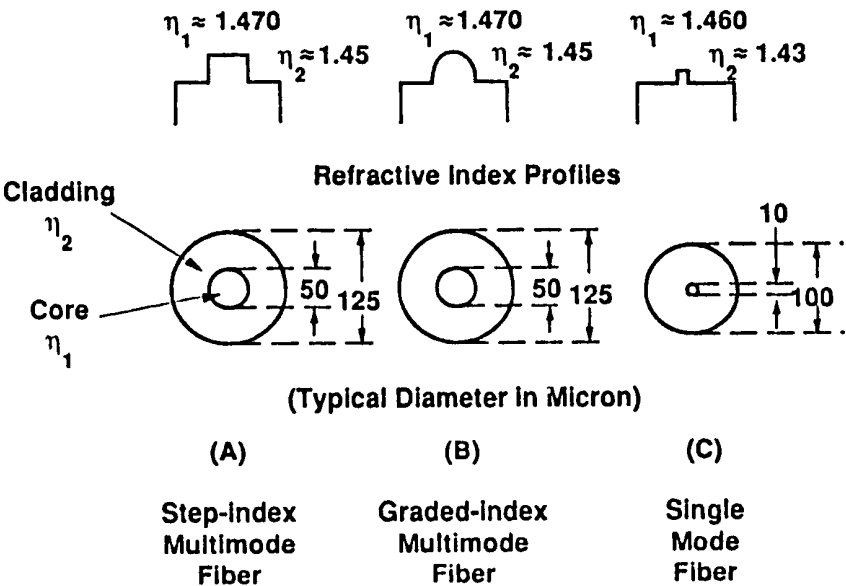


Figure 16.8. The three basic types of optical fibers for communication.

Step-Index Multimode. The step-index multimode fiber has a sharp difference between the index of refraction of the core and that of the cladding (Fig. 16.8a). Light propagation in such a fiber is

shown in Fig. 16.9. Only the light rays that enter the fiber within the angle of acceptance travel entirely within the core. Others, entering at a higher angle, escape the fiber. Rays entering parallel to the axis travel the shortest distance, while those entering at an angle to the axis (within the angle of acceptance) travel farther and arrive later at any given point. This delay causes intermodal distortion.

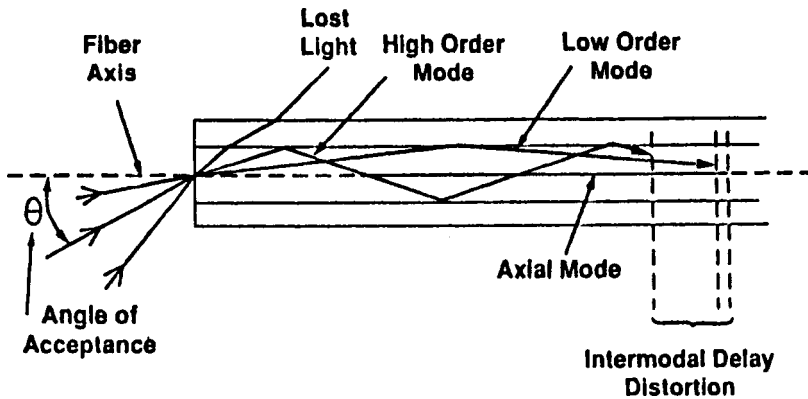


Figure 16.9. Light propagation in a multimode step-index fiber.

Graded Multimode. In the graded-index multimode fiber, the index of refraction varies parabolically across the fiber (Fig. 16.8b) and is known as a “gradient index” or GRIN. In such a gradient, the speed of light (which is a function of the index of refraction) increases with the distance from the center of the core. This greater velocity compensates for the longer path of the off-axis rays and intermodal distortion can be avoided by careful and exacting grading of the refractive index.

Single Mode. The single-mode fiber has a step-index profile (Fig. 16.6c) and a small core diameter (typically 10 μm) such that only one mode can travel through it. This is now the preferred system, particularly for long-distance transmission. The normal light source for multimode fibers is the light-emitting diode (LED). But

LED: do not have sufficient power for single mode fiber applications which, because of the smaller cross-sections, require more powerful lasers. The CVD of LED and laser materials is described in Ch. 15.

The control of impurities in the glass, such as copper, iron, vanadium, and hydroxyl groups, is extremely important since these are the major cause of signal attenuation. These impurities must be limited to a maximum in the 10^9 range. Such low degree of impurity is now achieved routinely by CVD. Good refractive index design and impurity control have resulted in a considerable improvement in fiber performance. Single-mode fibers commonly transmit over long distances (hundreds of km between repeaters) with minimum attenuation. Current fibers provide 250 times the information capacity of equivalent size copper wires and the standard production optical cable can now carry 1.8 million telephone calls at the same time. This is 36 times the capacity of similar optical cables produced in 1979, and is evidence of the considerable progress made in this field.

5.2 CVD Production of Optical Fibers

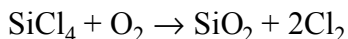
Two major processes are available for the production of optical fibers: (or liquid phase) and CVD. Solgel is being evaluated but has yet to evolve into a viable production process for that application.

The direct melt process economically produces thick optical fibers (250–400 μm in diam.), which is advantageous, but their relatively high attenuation (3–20 dB/km) due to impurities is not. As a result, they are limited to short distance multimode applications.

CVD yields fibers with low loss (< 0.5 dB/km) which are suitable for both mono- and multimode long-distance applications. It has emerged as the strongest technology for high-volume, low-cost production.^[18]

Two variations of the general process are used. The first is a classical thermal CVD method. The reactants are usually the halides, i.e., SiCl_4 , GeCl_4 , and POCl_3 with Cl_2 , O_2 , and $\text{C}_2\text{Cl}_2\text{F}_2$. These

reactants are maintained at extremely low levels of impurities. The basic reaction to deposit the core is:



The same reaction is used with the dopants to form the cladding. A schematic diagram of the deposition system is shown in Fig. 16.10. The reaction occurs inside a rotating silica tube which is heated by a traversing heat source, usually an oxyhydrogen burner as shown in Fig. 16.11. The SiO_2 is produced in the form of soot which deposits just ahead of the burner in a porous mass which is fused to a sintered glassy layer by the heat of the traveling burner. The cladding material is first deposited, followed by the core. The tube is then collapsed at 1800°C to form a solid preform rod which is next heated (usually in a O_2/H_2 flame) and drawn to a diameter of approximately $100\text{ }\mu\text{m}$. The original indices of refraction of the preforms are retained in the drawn fiber. The technique is used to produce step-index or graded-index multimode or single mode fibers.

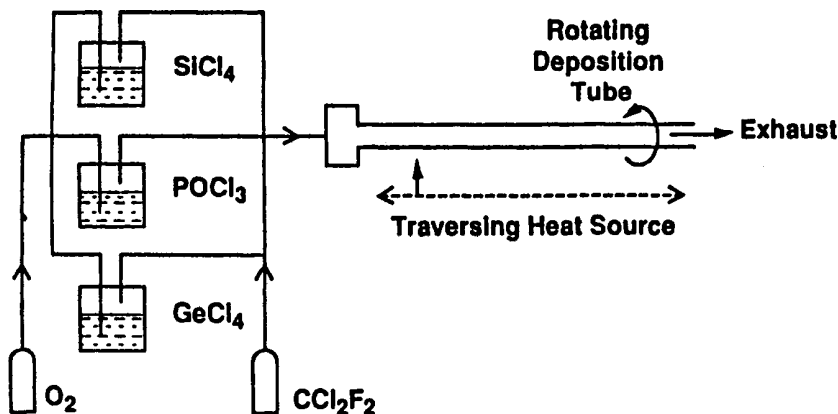


Figure 16.10. Diagram of deposition apparatus for optical fibers.

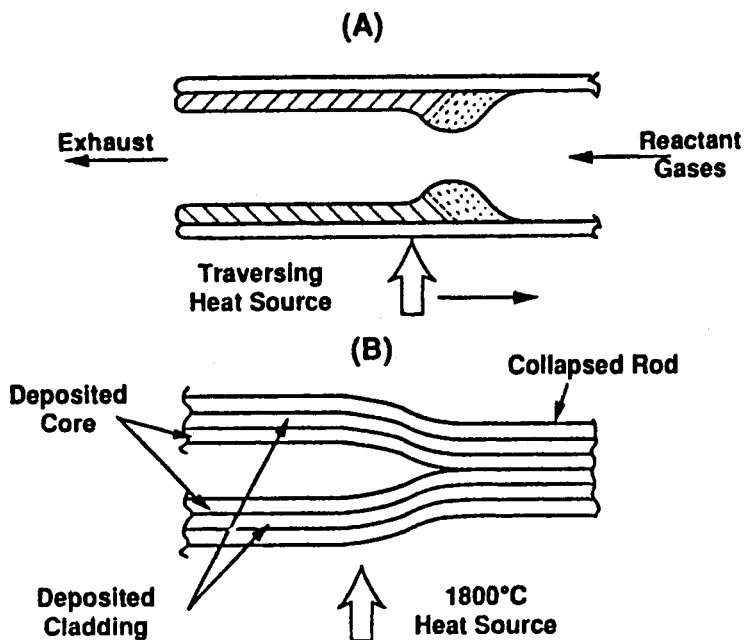


Figure 16.11. (a) Deposition of cladding and (b) tube collapse in optical fiber production.

A similar deposition system uses a plasma which is produced by a traveling microwave cavity. No other source of heat is required. The deposition system is shown schematically in Fig. 16.12. The reactants are the same as in the thermal CVD process. Pressure is maintained at approximately 1 Torr. In this case, the deposition occurs at lower temperature, no soot is formed and a compact glass is produced directly. A main advantage of this method is the more accurate grading of the refractive index of the cladding material.

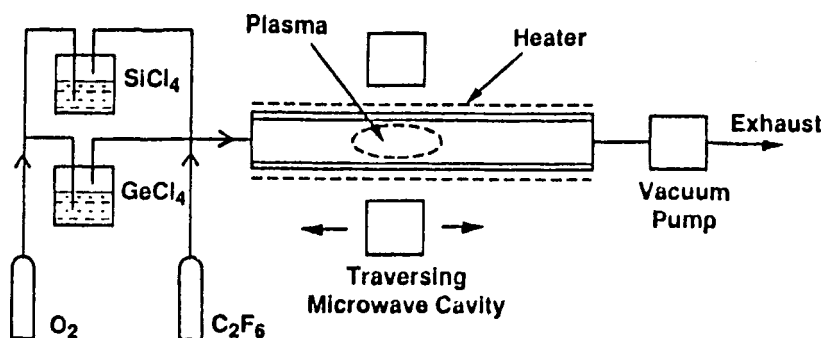


Figure 16.12. Diagram of plasma-CVD apparatus for optical fiber production.

5.3 Infrared (IR) Transmission

Another application of fiber optics with great potential is transmission in the IR region (as opposed to the transmission in the optical region) which is being investigated extensively in the US and abroad.^[19] Glass is essentially a disordered material and as such scatters a certain amount of light due to random changes in composition and density. This scattering varies inversely with the fourth power of the wavelength. Thus, it would be advantageous to use longer wavelengths such as in the infrared. In addition, the absorption of light caused by electronic excitation is less at lower frequency (longer wavelength). Transmission in the IR region is therefore very desirable and it has been calculated that, if a suitable glass is developed, an IR signal could cross the Atlantic Ocean without amplification.

The main problem in developing fibers for IR transmission is that silica glass is not transparent in that area of the spectrum. Suitable materials include the selenides and other chalcogenide glasses (particularly for the CO_2 laser light source) and the fluorohafnate glasses. In addition, materials such as zirconium fluo-

ride (ZrF_2), arsenic triselenide (As_2Se_3), and potassium iodide (KI), contain atoms of relatively high mass that are weakly bonded and thus transparent to IR from 2 to 5 μm . Fluoride fibers are particularly attractive because they are very flexible and ideal for medical applications such as laser angioplasty. However, the CVD technique of making fibers from these materials is still in the early stage of development.

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17

CVD in Wear-and Corrosion-Resistant Applications

1.0 INTRODUCTION

CVD coatings are used extensively in applications requiring resistance to wear and corrosion, often over a wide range of temperature. As mentioned in Ch. 1, these coatings and their substrates can be considered as composites which provide unique combinations of properties.

An example is the coating of a cutting tool such as a twist drill. The drill must be made of a tough and strong material, such as high speed-tool steel, that is able to withstand the stresses associated with drilling, yet its surface must be very hard and chemically resistant to withstand abrasion and corrosion. However, hardness and toughness are inverse properties and no single material can have both. A solution is to coat the steel body with a refractory metal carbide or nitride which protects the steel substrate from high temperature oxidation and reaction with the material to be cut and provides the necessary hardness and wear resistance.

Wear and corrosion protection can be provided by the well-established techniques of hard-facing and plating or by surface-modification processes such as boriding, nitriding, carburizing, and ion implantation. The protection these processes afford is adequate in most environments but may fail over a period of time if the conditions are too severe.

Another useful and common technique is plasma spraying, which has the drawback of requiring thick deposits to insure adequate protection. Often extensive grinding and polishing are needed. Other techniques, such as sputtering, provide excellent protection but are limited by their line of sight characteristic, although the use of magnetron sputtering with multiple targets partially offsets this limitation (see Appendix).

CVD suffers these limitations to a lesser degree and, as a result, is being used increasingly in many industrial applications, particularly those operating in extreme conditions. It is often the best solution to severe problems of erosion, friction, or hot corrosion. A special case must be made for the coating of cutting tools, which is a major industrial application of CVD and is reviewed separately in Ch. 18.

2.0 WEAR MECHANISMS

Surface wear is defined as the deformation and loss of surface material as the result of a mechanical, thermal, or chemical action. These three mechanisms can act singly but are more often found in combination, which may make the wear process very difficult to analyze. Materials for wear protection have different responses to each of these wear mechanisms and, consequently, no universal wear material exists. To select the optimum material or combination of materials, it is essential to determine the cause and the mechanism of the wear as accurately as possible. The selection can then be made of the best and most cost-effective material.

2.1 Mechanical Wear

Mechanical wear is caused by the action of mechanical forces. A wear surface, viewed under high magnification, shows an irregular topography generally characterized by a series of ridges and grooves. Contact with another surface occurs on the ridges, which become highly stressed since they carry all the load. Particles on both surfaces tend to fuse together and be removed by adhesive and shear failure. Abrasive wear is a similar mechanism which results from hard particles gouging the softer surface. The wear surface may also be weakened by the applied stresses that cause fracturing along the dislocations in the lattice structure.

Beside adhesive and abrasive wear, two other wear mechanisms must be mentioned:

- Fatigue wear, which is caused by the formation and propagation of surface cracks that typically occur in ball bearings and friction gears.
- Cavitation wear, which occurs when a solid such as ship propeller moves at high speed in a liquid, leading to the formation of bubbles, which are a major cause of surface erosion.

A direct relationship is found between the hardness of a material and its ability to withstand mechanical wear, and as a rule the harder the material, the greater is its wear resistance. A related factor is that harder materials usually take a better polish and, as a result, the wear due to surface roughness mentioned above can be minimized. Choosing material combinations with a low coefficient of friction is also an important factor in reducing mechanical wear.

2.2 Corrosive Wear

Corrosive wear results from a chemical reaction of the wear surface with the environment. In this section, only corrosion that occurs in conjunction with mechanical wear is considered. Purely corrosive wear is reviewed in Sec. 4.0 below. The chemical resistance of a given coating material must be assessed if the application involves a corrosive environment. A typical example is the environment found in deep oil and gas wells (over 500 m.), which usually contain significant concentrations of CO_2 , H_2S , and chlorides. The corrosive effect of these chemicals is enhanced by the high temperature and pressure found at these great depths.

TiC , TiN , and Si_3N_4 are usually inert to most corrosive and oxidizing environments unless the application involves high temperatures, in which case oxides such as SiO_2 , Al_2O_3 , and TiO_2 are preferred. Yet, any coating, even if completely resistant to corrosion by itself, is of little value if pores or microcracks are present or if it is highly stressed, which makes it prone to adhesive and cohesive failure.

2.3 Temperature Effects

All materials, with a few notable exceptions such as graphite, undergo an accelerated degradation of their properties with increasing temperature. This is particularly true of chemical resistance and mechanical properties such as strength and hardness as shown for refractory carbides in Fig. 17.1. It should be noted that pure tungsten carbide (WC) retains its hardness up to 600°C while the hardness of other carbides decreases rapidly with rising temperature. Diffusion of one material into the other also increases rapidly with increasing temperature, particularly in materials that have poor thermal stability.^[1]

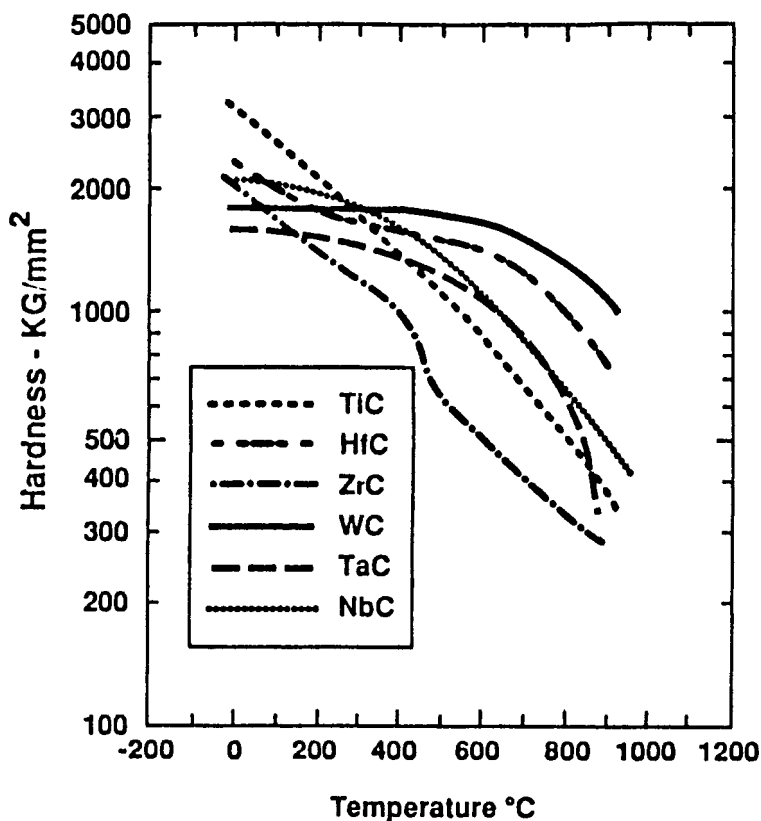


Figure 17.1. Hardness of refractory carbides as a function of temperature.

3.0 CVD MATERIALS FOR WEAR- AND CORROSION-RESISTANCE

3.1 Wear- and Corrosion-Resistance Materials

The CVD coating materials for wear and corrosion resistance consist mostly of carbides and nitrides and, to a lesser degree, borides. Table 17.1 compares the relative properties of these materials.

Table 17.1
Relative Properties of Carbides, Nitrides, and Borides

	High	Medium	Low
Melting Point	C	B	N
Stability	N	C	B
Thermal Expansion	N	C	B
Hardness	B	C	N
Toughness	N	C	B
Reactivity	B	C	N
Adhesion to substrate	B	C	N
C = carbides			
N = nitrides			
B = borides			

The number of CVD coating materials for wear and corrosion resistance is relatively small. The most important are as follows:^[1]

Titanium Carbide. TiC, with its great hardness and wear resistance, is particularly suitable to reducing mechanical and abrasive wear. However, it is susceptible to chemical attack and is not a good diffusion barrier.

Titanium Nitride. TiN is chemically stable. TiN forms an excellent diffusion barrier and has a low coefficient of friction. As such, it is well suited for reducing corrosion, erosion, and galling. It is used extensively as a coating for gear components and tube- and wire-drawing dies.

Titanium Carbonitride. Ti(C,N) is a solid solution of TiC and TiN and combines the properties of both materials. It offers excellent protection against abrasive wear and has good lubricating characteristics. It is used to coat tools and dies for the processing of ceramics, graphite, and filled plastics.

Chromium Carbide. Cr₇C₃ has excellent corrosion and oxidation resistance. It is rarely used alone but mostly in combination with TiC and TiN as a base layer.

Silicon Carbide. SiC has low thermal expansion, high hardness, and good resistance to oxidation. It is used extensively in the coating of graphite and carbon to impart wear and oxidation resistance.

Titanium Boride. TiB₂ is extremely hard, corrosion resistant, and provides good protection against abrasion.

Aluminum Oxide. Al₂O₃ has high strength and excellent stability and oxidation resistance.

Diamond-like Carbon. DLC is very hard and chemically inert but the coating is usually highly stressed in thicknesses greater than 1 μm. Its production applications are relatively recent but it is already used in textile machinery, bearing surfaces, measuring instruments, air bearings, precision tooling, gears, fluid engineering systems, engine components, nozzles, and rotating equipment.^[2]

The characteristics and properties of these materials are summarized in Table 17.2.

The comparative wear rate of some of these materials is shown in Fig. 17.2. The wear was obtained with aluminum oxide powder in a jet abrader.^[3] Hard coating materials such as TiB₂, TiC, or SiC have extremely small wear rates.

The materials listed in Table 17.2 are often used as multilayer structures to take advantage of the strongest characteristics of each.

Other CVD-produced materials used to a lesser extent or on an experimental basis for wear, erosion, and corrosion applications include the following:

- (Ti,Al)N has essentially the properties of TiN but with much higher oxidation resistance. It is now deposited by sputtering and its deposition by CVD is being investigated.
- Boron carbide (B₄C) is extremely hard and is used where maximum resistance to erosion is required. It has good nuclear properties (see Ch. 9).
- Hafnium nitride (HfN) has good oxidation resistance and is developed as a cutting tool material (see Ch. 10).^[4]

- Molybdenum disulfide (MoS_2) and tungsten diselenide (WSe_2) are used for their excellent dry lubricant properties.
- Polycrystalline diamond, the hardest material, may provide the best wear and erosion resistance material once the deposition problems are solved and it has become commercially viable (see Ch. 7).

Table 17.2
Relevant Wear and Corrosion Properties of CVD Coating Materials (at 25°C)

	Hardness kg/mm^2	Thermal Conduc- tivity W/cm K	Coeff. of Thermal Expansion $\text{m/m}\cdot^\circ\text{C}\cdot 10^{-6}$	Remarks
TiC	3200	0.17	7.6	high wear and abrasion resistance low friction
TiN	2100	0.33	9.5	high lubricity stable and inert
Ti(CN)	2500–3000	0.2–0.3	app. 0.8	stable lubricant
Cr_7C_3	2250	0.11	10	resists oxidation to 900°C
SiC	2800	1.25	3.9	high conductivity shock resistant
TiB_2	3370	0.25	6.6	high hardness and wear resistance
Al_2O_3	1910	0.34	8.3	oxidation resistant high stability
DLC	3000–5000	2.0		high hardness, high thermal conductivity

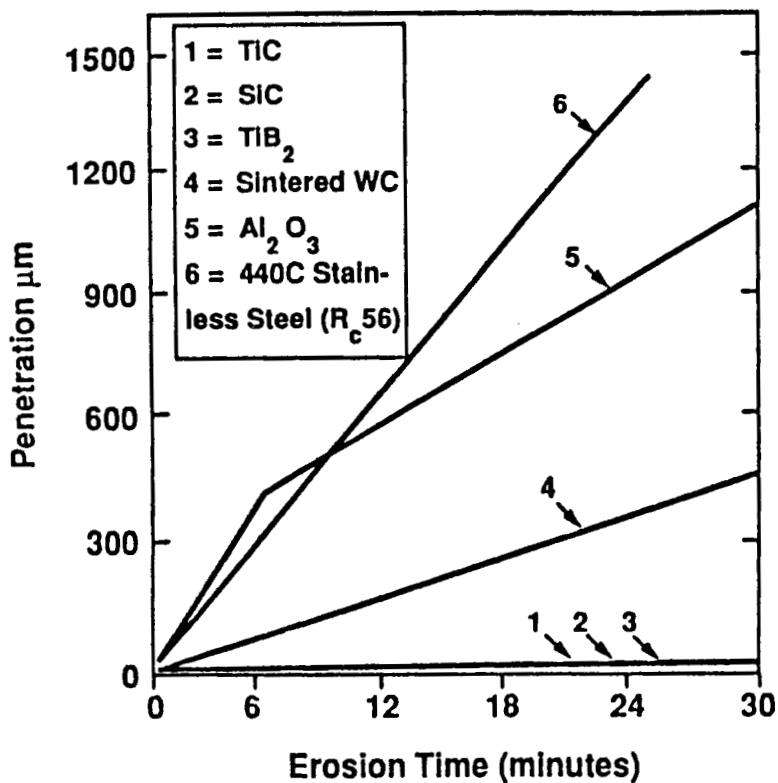


Figure 17.2. Comparative wear rate of selected hard materials.

3.2 Wear and Corrosion Resistance Applications of CVD Coatings

Existing development and production applications in wear, erosion and corrosion protection are shown in Table 17.3.

Table 17.3
Wear, Erosion, and Corrosion Applications of Refractory Carbides and Nitrides

Metal Forming (non-cutting):

Tube and wire drawing dies (TiN)
Stamping, chamfering and coining tools (TiC)
Drawing punches and dies (TiN)
Deep drawing dies (TiC)
Sequential drawing dies (Cr₇C₃)

Ceramic and Plastic Processing:

Molding tools and dies for glass-filled plastics (Ti(C,N))
Extrusion dies for ceramic molding (TiC)
Kneading components for plastic mixing (TiC)

Chemical and General Processing Industries:

Pump and valve parts for corrosive liquids (SiC)
Valve liners (SiC)
Positive orifice chokes (SiC)
Packing sleeves, feed screws (TiC)
Thermocouple wells (SiC)
Valves for coal-liquefaction components (TiB₂)^[5]
Heating elements (SiC)
Paper-processing rolls and shafts (TiC)
Solder handling in printed-circuit processing (TiC, TiN)

Machine Elements:

Gear components (TiN)
Stainless-steel spray-gun nozzles (TiC)
Components for abrasive processing (TiC)

Metal Coatings:

NbC and TaC for the protection of Nb and Ta metals

These materials are produced in monolithic form or as coatings. The coatings are generally applied by CVD on ceramic substrates and by sputtering, electron-beam evaporation, or ion-beam assisted deposition on steel substrates (see Appendix).

Ball Bearings. A typical coating application for wear resistance is found in ball bearings. In some applications, steel-ball bearings do not have the necessary hardness and corrosion resistance. Microwelds tend to occur between the balls and the race which roughen the surfaces and contaminate the lubricant. TiC coatings by CVD on steel balls (usually SAE 52100 or AISI 440C) provide much increased hardness, a smoother surface, and a lower coefficient of friction.^{[6][7]} In some cases, solid Si_3N_4 balls are replacing steel balls because of their high hardness, chemical resistance, and low density (a feature important in high-speed applications).^[8] Further improvement results from coating the silicon nitride with CVD TiN.

Typical applications of coated ball bearings are:^[9]

- Spin-axis gyroscope with oil lubrication (TiC).
- Bearings in space vehicles operating in vacuum with fluid or solid lubricant (TiC).
- Balls for high-speed machine-tool bearings (Si_3N_4).
- Balls for valves of oil-field sucker-rod pumps (Si_3N_4).

In this particular example as in many others, a proper analysis of cost is a crucial factor. An example is the production of balls for ball bearings. Coated ball bearings (or monolithic silicon nitride) greatly outperform steel balls but their cost is considerably higher. Steel balls in passenger-automobile applications are satisfactory and normally last the life of the car and the far-longer life of the ceramic balls is not needed.

4.0 CVD IN CORROSION-RESISTANT APPLICATIONS

In many respects, the problems of corrosion are similar to those of wear and erosion reviewed above, and often a corrosion application also requires resistance to wear and erosion. In this

section, CVD applications where corrosion resistance is the major factor are reviewed.

Corrosion is defined as the wearing of a surface by chemical action. It is usually a slow and often unnoticed phenomenon, yet it is all pervasive and incredibly costly. In the US alone, the corrosion of metals is estimated to cost over ten billion dollars a year for replacement, repairs, and maintenance.

Protecting a surface from corrosion by coating can be accomplished by a number of well-established processes which include paints, metal plating (with zinc or cadmium), diffusion, thermal spraying, and, more recently, vapor deposition processes. Of these physical vapor deposition (PVD) is used extensively in corrosion protection. Typical applications are:

- Aluminum metallizing of steel or plastics by evaporation.
- Alloy coating of turbine components by electron-beam evaporation and sputtering.
- Sputter coating of watches, frames for eyeglass and similar items with titanium nitride.

CVD is a relatively newcomer in the area of corrosion protection but is making rapid strides and may soon become a serious competitor to PVD and other coating processes.

4.1 CVD Metals for Corrosion Resistance Applications

The range of chemical reactivity of metals is wide, from the inertness of the platinum group to the extreme reactivity of some alkali metals. The order of metal reactivity follows essentially the order of the electrochemical series which is shown in Table 17.4 for the metals commonly deposited by CVD.

Table 17.4
Electrochemical Series of the CVD Metals

Metal	Electrode Potential (V)	Metal	Electrode Potential (V)
Magnesium	-2.38	Hydrogen	(0)
Aluminum	-1.67	Rhenium	0.300
Titanium	-1.63	Copper	0.343
Manganese	-1.185	Silver	0.799
Niobium	-1.09	Palladium	0.82
Zinc	-0.763	Platinum	1.118
Tantalum	-0.750	Iridium	1.156
Chromium	-0.557	Gold	1.42
Iron	-0.44		
Cadmium	-0.402		
Cobalt	-0.28		
Nickel	-0.23		
Molybdenum	-0.20		
Tin	-0.141		
Tungsten	-0.119		

The metals above hydrogen in the series react with water to form hydrogen, at room temperature for the alkali metals, at 100°C with steam for magnesium and zinc, and at red heat for manganese and cobalt.

Oxidation is the largest cause of corrosion of metals. The conversion of a metal into an oxide by the direct combination with oxygen is the most common form of oxidation. The best known example is the rusting of steel. Oxidation, in the more general context, is the result of the increase of positive charge of an ion. Reduction is the reverse of oxidation. The most common oxidizing agents are oxygen, ozone, peroxides, the oxy-acids such as nitric, chromic and chloric acids, the halogens, and many others.

The resistance of metals to oxidation varies considerably. Gold and most metals of the platinum group do not react at room temperature or at least the reaction rate is extremely slow. Copper,

lead, tin, iron, chromium, and aluminum oxidize slowly and a continuous thin film of impermeable oxide is formed which essentially prevents further oxidation. The oxide formed on iron, zinc, and magnesium is discontinuous and oxidation continues linearly.

The rate of oxidation increases with temperature. Oxygen diffusion becomes more rapid, the oxide film becomes thicker and eventually cracks and spalls off due to internal stress. Oxidation then becomes continuous and rapid.

4.2 CVD Borides for Corrosion-Resistance Applications

Borides are relatively inert, especially to non-oxidizing reagents. They react violently with fluorine, often with incandescence. Reaction with other halogens is not as violent and may require some heat. Resistance to oxidation, acids, and alkalis is summarized in Table 17.5. In oxidation conditions, a layer of boric oxide is formed on the surface which passivates it to some degree. Boric oxide melts at 450°C and vaporizes at 1860°C. It offers good protection up to 1500°C in a static environments but it has low viscosity at these temperatures and tends to flow under stress and the protection it offers is limited.^{[10][11]}

Table 17.5
Selected Chemical Properties of Transition-Metal Borides

Boride	Approx. Oxidation Threshold (°C)	Resistance to Acids			Resistance to Alkalis
		HCl	H ₂ SO ₄	HNO ₃	
HfB ₂	750	poor	poor	poor	poor
Mo ₂ B ₅	500	poor	good	poor	poor
NbB ₂	500	good	good	good	poor
TaB ₂	500	good	good	good	poor
TiB ₂	550	poor	poor	poor	poor
W ₂ B ₅	500	good	good	poor	poor
ZrB ₂	650	poor	poor	poor	poor

Borides are generally resistant to molten metals, at least to those that do not readily form borides, such as copper, zinc, magnesium, aluminum, tin, lead, and bismuth. TiB_2 is especially resistant to molten aluminum and, as such, is used in crucibles for evaporation of the metal.

4.3 CVD Carbides for Corrosion-Resistance Applications

The refractory carbides have very high melting points and low vapor pressures and are very stable in vacuum or inert atmosphere. They are generally not attacked by hydrogen or nitrogen even at high temperature. They react with the halogens at high temperatures. Reaction threshold temperature for B_4C and SiC in fluorine is 700°C .

TiC has good resistance to sulfuric acid.^[12] A passivating oxide layer is formed up to a potential of 1.8 V at which point corrosion becomes severe. TiC is also very resistant to sea water, neutral industrial waste waters, and human sweat. Cr_7C_3 is even more corrosion resistant and is used extensively as a passivation interlayer.

Carbides oxidize readily although less rapidly than the nitrides but more so than the borides. Oxidation becomes more rapid going from the Group IV carbides (TiC , ZrC , HfC) to those of Group VI (Cr_3C_7 , MoC , WC). In some cases, a protective film of the metal oxide is formed. Such is the case with SiC , as reviewed in Sec. 5.7 below.

The carbides are generally not resistant to molten slags and fused salts. Their resistance to molten metal is usually poor. For instance, TiC is attacked by nickel, cobalt, chromium, and silicon. SiC is attacked by aluminum.

4.4 CVD Nitrides for Corrosion-Resistant Applications

The thermal and chemical stability of the refractory metal nitrides is high with those of Group IV (titanium, zirconium, and hafnium). It decreases with those of Group V (vanadium, niobium, and tantalum) and is low with those of Group VI (chromium, molybdenum, and tungsten). CVD TiN, ZrN, and HfN are the most commonly used. They provide a good barrier to diffusion. Their resistance to acids is generally good, at least at room temperature. However, they are decomposed by boiling alkali solutions or fused alkali. Their oxidation resistance is poor. TiN is resistant to sea water and human sweat. It has a pleasing gold appearance and for that reason is used extensively in jewelry and similar applications.

Other useful refractory nitrides for corrosion protection are silicon nitride (Si_3N_4) and boron nitride (BN). Silicon nitride has good corrosion resistance and is not attacked by most molten metals as shown in Table 17.6 (see Ch. 10).

Table 17.6
Resistance of Silicon Nitride to Molten Metals

Metal	Temperature (°C)	Time (hr)	Degree of Attack
Al	800	950	none
Al	1000	100	none
Pb	400	144	none
Sn	300	144	none
Zn	550	500	none
Mg	750	20	slight
Cu	1160	7	severe

Boron nitride is one of the most outstanding corrosion-resistant materials. It is inert to gasoline, benzene, alcohol, acetone, chlorinated hydrocarbons and other organic solvents. It is not wetted by molten aluminum, copper, cadmium, iron, antimony, bismuth, silicon, germanium, nor by many molten salts and glasses. It is used extensively as crucible material, particularly for molten metals, glasses and ceramic processing.

4.5 CVD Oxides for Corrosion-Resistance Applications

The main characteristic of refractory oxides is their excellent resistance to oxidation. Their brittleness however makes them prone to thermal shock with the exception of silica which has a compensating low coefficient of thermal expansion. The chemical resistance of the major oxides deposited by CVD is rated in Table 17.7.

Table 17.7
Chemical Properties of CVD Refractory Oxides

	<u>Stability to</u>				
	Reducing Atm	Carbon	Acid Slags	Basic Slags	Molten Metals
Alumina	good	fair	good	good	good
Hafnia	good	fair	good	poor	good
Silica	poor	poor	good	poor	poor
Titania	poor		good	poor	
Zirconia	good	fair	good	poor	good

4.6 CVD Silicides for Corrosion-Resistance Applications

The major characteristics of most silicides, particularly MoSi_2 and to a lesser degree TiSi_2 and WSi_2 , is their excellent oxidation resistance. The formation of a strong adherent oxide layer protects the silicide from further oxidation, up to 1900°C in the case of MoSi_2 (see Ch. 12). This characteristic is used to good advantage in the design and manufacture of heating elements for high-temperature furnaces. Element life of several hundred hours at 1800 – 1900°C is reported. MoSi_2 is stable in SO_2 , CO_2 , N_2O , and hydrocarbons up to 1000°C and in N_2 and CO_2 up to 1500°C . Resistance to acids is generally low.

4.7 Oxidation Protection of Carbon-Carbon Composites

Aerospace materials are now being operated at or near their capacities with regard to temperature, stress and environment, especially in applications such as turbine-engine components. Their operational limits must be extended in order for performance improvements to be realized. The material most likely to be able to meet the new performance requirements is carbon either hot pressed or especially in the form of carbon-carbon composite, a material comprising carbon fibers in a carbon matrix. This composite has the highest specific strength of any material above 1000°C .^[2] It has a small thermal expansion and is able to withstand the thermal shock caused by extremely high heating rates. However, like all carbon material, it oxidizes rapidly above 600°C and an oxidation protection is a necessity. This is usually provided by silicon carbide which is applied by pack cementation or by CVD, usually in combination with other materials such as boron which promotes self-healing characteristics.

Present oxidation-protection systems are based on silicon carbide (SiC), which is applied by pack cementation or by chemical-vapor infiltration (CVI) (see Ch. 4).^[13] Boron, zirconium, and other

materials are sometimes added to the matrix of the composite or as interlayers to impart self-healing characteristics and extend the maximum operating temperature. During oxidation, a vitreous silica (SiO_2) layer is formed which provides good oxidation protection, but only to approximately 1500°C .

Any operation above that temperature is likely to result in failure, even after a short period of time. This is due to the decomposition of the SiC which may occur well below its melting point and to the formation of the volatile suboxide SiO, which evolves rapidly above 1600°C at low oxygen partial pressures by simple gasification. Another reason is the rapid decrease in viscosity of the SiO_2 protective layer with increasing temperature. This would be a severe problem with components subjected to high dynamic loads, such as a high-velocity gas stream in the case of turbine blades. A conservative design for extended life dictates an upper temperature limit of about 1370°C for a silicon carbide-based oxidation protection system.

A refractory coating has been developed that provides oxidation protection for carbon-carbon composites to 1800°C for extended periods (hours) and to 1900°C for shorter periods, thus substantially raising the effective upper temperature limit for carbon-carbon. This coating is a multilayered structure of mixed hafnium carbide and silicon carbide obtained by CVD, formed by alternating the deposition of HfC and SiC at regular intervals (see Ch. 7). During oxidation, a thin adherent layer of a mixed oxide is formed on the coating which provides an effective barrier to oxidation of the substrate. This mixed oxide is composed of hafnium oxide (HfO_2) and silicon oxide with hafnium silicide.^[10]

Other refractory oxides that can be deposited by CVD have excellent thermal stability and oxidation resistance. Some, like alumina and yttria, are also good barriers to oxygen diffusion providing that they are free of pores and cracks. Many however are not, such as zirconia, hafnia, thoria, and ceria. These oxides have a fluorite structure, which is a simple open cubic structure and is particularly susceptible to oxygen diffusion through ionic conductivity. The diffusion rate of oxygen in these materials can be considerable.^[14]

Iridium Coating for Spacecraft Rocket Nozzles. The coating of rocket nozzles with iridium is a good example of the ability of CVD to provide a complete composite material, in this case a structural refractory shell substrate coated with a corrosion- and oxidation-resistant component. The device is a thruster rocket nozzle for a satellite. The rocket uses a liquid propellant which is a mixture of nitrogen tetroxide and monomethyl hydrazine.

The nozzle of original design was fabricated from a niobium alloy coated with niobium silicide and could not operate above 1320°C. This was replaced by a thin shell of rhenium protected on the inside by a thin layer of iridium. The iridium was deposited first on a disposable mandrel, from iridium acetylacetonate (pentadionate) (see Ch. 6). The rhenium was then deposited over the iridium by hydrogen reduction of the chloride. The mandrel was then chemically removed. Iridium has a high melting point (2410°C) and provides good corrosion protection for the rhenium. The nozzle was tested at 2000°C and survived 400 cycles in a high oxidizer to fuel ratio with no measurable corrosion.^[15]

Other CVD Corrosion-Resistance Applications. The following is a listing of typical applications where CVD is used either in production or experimentally for corrosion protection.

- SiO_2 and Si_3N_4 are deposited on steel by plasma CVD at low temperature on a continuous basis for oxidation protection in combination with ion plating and sputtering.^[16]
- CVD SiO_2 provides effective protection for stainless steel in CO_2 up to 1000°C.^[17]
- Molybdenum heat pipes, coated with CVD SiC , can operate in the temperature range of 830–1130°C in an oxidizing atmosphere.^[18]
- Copper plates coated with TiB_2 by CVD have shown good resistance to corrosion by sea water and erosion by sand.^[19]

5.0 DECORATIVE APPLICATIONS OF CVD

Coatings of refractory carbides and nitrides and more recently carbon and DLC are used extensively in decorative applications on jewelry, eyeglasses, and similar products in attractive colors such as gold (TiN) and metallic grey, or charcoal (DLC, CrN, and TaN). They provide a surface which is hard and wear resistant, sweat resistant and, in the case of gold, less costly. They are usually applied by cathode sputtering and less frequently by CVD.

6.0 NUCLEAR APPLICATIONS OF CVD

6.1 Nuclear-Fission Applications

The protection of components against nuclear radiation is a critical factor in the design of nuclear-fission components.^[20] CVD is used extensively in this area, particularly in the coating of nuclear fuel particles such as fissile U-235, U-233, and fertile Th-232 with pyrolytic carbon. The carbon is deposited in a fluidized-bed reactor (see Ch. 4). The coated particles are then processed into fuel rods which are assembled to form the fuel elements.

The function of the carbon coating is to contain the by-products of the fission reaction, thereby reducing the shielding requirements. It also protects the nuclear fuel from embrittlement and corrosive attack and from hydrolysis during subsequent processing steps. CVD coatings of alumina deposited at 1000°C and beryllia deposited at 1400°C have also been studied for that purpose.^[21]

6.2 Nuclear Fusion Applications

CVD is used in many experimental coatings for fusion devices. Refractory materials with very high chemical stability and low

atomic number are preferred, such as TiB_2 , TiC , SiC , carbon, and boron. These materials must be able to withstand very severe thermal shock.^{[22][23]} The following applications have been reported in the literature.

- TiC coating on graphite for limiters and neutral beam armor.
- Boron and B_4C deposited by plasma CVD on graphite for wall armor protection in fusion reactors.^[24]
- *In situ* deposition of carbon (i.e., within the fusion reactor chamber which becomes the CVD reactor).
- Coatings for inertial confinement microsphere targets comprised of multilayers of Be, Au, Pt, and Ta.^[25]

7.0 BIOMEDICAL APPLICATIONS OF CVD

Materials used in body implants must meet several essential requirements such as tissue compatibility, enzymatic and hydrolytic stability. They must also be chemically resistant and have good mechanical properties. They must not be toxic, or the surrounding tissue will die. They must be resistant to the body fluids which usually have a high percentage of chloride ions. They must be biologically active if an interfacial bond is to be achieved. In some cases, they must be able to withstand continued high mechanical stresses for many years.^[26]

Biomedical materials include ceramics such as the biologically active hydroxylapatite and tricalcium phosphate, and high-strength metals such as titanium alloys.^[27] These materials are not produced by CVD as this time, except on an experimental basis. CVD, however, is the major process used in the production of another very important biomedical material, i.e., isotropic

carbon.^{[28][29]} In fact, more implants are made from isotropic carbon than from any ceramic material.

Isotropic carbon is obtained by the pyrolysis of a hydrocarbon, usually methane, at high temperature (1200–1500°C) in a fluidized bed on a graphite substrate.^[30] Under these conditions, a turbostratic structure is obtained which is characterized by very little ordering and an essentially random orientation of small crystallites. In contrast to graphite which is highly anisotropic, such a structure has isotropic properties (see Ch. 7). Isotropic carbon is completely inert biologically. Its properties are compared to alumina, another common implant material, in Table 17.8. Notable is its high strain to failure.^[28]

The major biological application of isotropic carbon is in heart valves. The material is performing well and several hundred thousand units have been produced so far. Other applications include dental implants, ear prostheses, and as a coating for in-dwelling catheters.

Table 17.8
Properties of Isotropic Carbon vs. Alumina

Properties	Isotropic Carbon	Alumina
Density, g/cm ³	2.1	3.89
Hardness, kg/mm ²	240–370	1500
Flexural strength, MPa	350	379
Young's modulus, GPa	28	372
Strain to failure, %	1.2	0.07–0.15
Fracture Toughness, MPa√m	2.5	4.2
Thermal expansion, m/m•°C x 10 ⁻⁶	4–6.5	3.2–8.3
Thermal conductivity, W/cm•°C	0.032	0.34
Electrical resistivity, Ω-cm	0.002	>10 ¹⁴

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18

CVD in Cutting-Tool Applications

1.0 INTRODUCTION

Many billions of dollars are spent every year in machining and the amount is increasing with the increasing use of hard-to-machine materials such as composites and refractory metals. This cost forms a large proportion of the total manufacturing cost and, in some industries such as airframe manufacturing, it is the major cost factor. This means a large market for machining equipment and for cutting tools. The global market for cutting tools was estimated at \$18 billion in 1994.^[1]

Coatings play a vital part in the cutting-tool industry and this is where CVD technology has made some of its most important gains. As an example, CVD films of titanium carbide on cemented carbide tools were first commercialized in the early 1960s and their use has continuously increased ever since. Today, the percentage of tools that are coated by either PVD or CVD depends on the type of tool as shown in Table 18.1 (in 1996).

Table 18.1
Percentage of Coated Tools per Tool Category

Carbide inserts and round tools	70–80%
High-speed steel	
• Hobs and gear cutting tools	80–90%
• Taps, end mills, and broaches	20–30%
• Drills	10–20%

2.0 CUTTING-TOOL REQUIREMENTS

2.1 Categories of Machining

Modern machining deals with an increasingly wide range of materials which includes, in addition to the traditional metals, high-chromium and nickel stainless steels, titanium, intermetallics, refractory metals, ceramics, glasses, fiber-reinforced composites, and many others. These materials have widely different properties. They react differently to machining and each presents a special machining problem.

The type of machining and its demands on the tool also vary greatly. Operations such as grinding, cutting, milling, drilling, tapping, and turning, all affect the tools in different ways. With such a wide variety of materials to be machined and large differences in machining conditions, it is obvious that no single tool material is able to meet all the requirements. A tool material suitable to cut aluminum differs from one which is suitable for drilling a carbide. The great flexibility provided by tool coatings has been particularly useful in meeting all these requirements and has been a vital factor in the development of modern machining.

2.2 Wear and Failure Mechanisms

The wear and subsequent failure of a cutting tool is a complex mechanism that usually involves a number of physical and chemical phenomena. Temperatures at the tool/workpiece interface (cutting edge) may reach up to 1200°C in a very short period of time. This creates a pronounced thermal shock and promotes oxidation of the tool surface and the diffusion of metallic constituents of the tool into the chip with a resulting loss of tool strength.

Additional important factors that contribute to failure are abrasive wear, adhesive wear, chipping, and plastic deformation. Abrasive wear is the result of the abrasion caused by the chip on the rake face of the tool as it moves past the workpiece. Adhesive wear galling is caused by the adhesion of a chip to the rake face of the tool due to a high temperature chemical reaction leading to localized welding. Plastic deformation is caused by the yield of the tool material under the high pressure and temperature encountered during the cutting operation.

Other wear mechanisms are flank wear and crater wear which occur mostly with cemented-carbide tools. Flank wear refers to the depression that is formed below the cutting edge on the side of the tool caused by the abrasive wear of the cemented carbide. TiC is particularly effective in reducing it. Crater wear occurs in the form of small depressions on the rake face behind the point of contact of the tool with the workpiece. Diffusion of the cobalt binder into the cutting chip usually occurs with crater wear. TiN is effective in reducing both diffusion and crater wear.^[2]

3.0 COATING PROCESSES AND SUBSTRATE INTERACTION

Both CVD and PVD are used extensively in the production of coatings for cutting-tool applications. The PVD processes include mag-

netron sputtering, reactive sputtering, cathodic arc, and ion-beam (see Appendix). A general comparison of CVD and PVD with respect to the coating of cutting tools is given in Table 18.2.^[3]

The selection of a coating process is much a function of the type of substrate to be coated as shown in the following section.

Table 18.2
CVD and PVD for Coating Cutting Tools

	CVD	PVD
Coating temperature, °C	850–1100 500 MOCVD	standard <500
Type of adhesion	diffusion	ion etching metallic bond
Degree of adhesion	excellent	moderate
Coating grain structure	fine to coarse	fine
Effect on substrate	significant on metals	generally not significant
Stress in coating	moderate	high
Sharp cutting edges	moderate	good
Coating thickness (μm)	1–10 or more	1–4

4.0 CUTTING-TOOL MATERIALS (SUBSTRATE)

The major cutting-tool substrate materials are high-speed tool steel, cemented carbides and, more recently, ceramics and diamond. The share of these materials of the total cutting-tool market is estimated as follows (in 1996):

High-speed steel	44%
Cemented carbides	49%
Ceramic & diamond	6%

4.1 High-Speed Tool Steel

High-speed tool steel is still a major material for cutting tools. It is inexpensive, it has high strength and toughness, and can be hardened to high Rockwell hardness (up to 70 Rc). Cutting tools have sharp edges for the purpose of shaving and generating a material curl, but in order for the tool to perform properly, this edge must remain sharp. In the case of uncoated tool steel, this sharp edge is lost rapidly.

High-speed tool steel has an austenizing temperature between 450 and 550°C. Heating above this transition temperature, such as would be required for coating by thermal CVD, leads to softening and requires a heat treatment for re-hardening. This may cause warpage and dimensional changes, in addition to increasing cost. Thus coating by high-temperature CVD, such as the halide-reduction reactions, is generally not practical or economical and most coatings on high-speed tool steel are done by PVD, specifically for brazed tools, end mills, threading inserts, reamers, and gear-cutting tools. Both CVD and PVD are used for milling inserts, grooving tools and drills, and CVD is used for turning inserts.

Work is under way to deposit TiN at lower temperature by plasma CVD and Ti(C,N) by MOCVD at temperature low enough to coat tool steel without degradation (see Ch. 10).^[4]

4.2 Cemented-Carbide Cutting Tools

This important group of cutting-tool materials is made from a carbide powder, usually tungsten carbide (WC), cemented under high pressure and temperature with a binder, usually cobalt. Cobalt-bonded WC has high-temperature strength and can be coated by thermal CVD with generally no problems, although too high a deposition temperature may lead to binder diffusion and the formation of a detrimental tertiary carbide $\text{Co}_6\text{W}_6\text{C}$, the so-called *eta phase*, at the WC/matrix interfaces. This leads to loss of strength and adhesion failure of the coating. Yet with proper controls, an excellent coating is obtained and today most cemented-carbide tools are coated by CVD, usually with multiple coatings.

4.3 Ceramic Cutting Tools

The use of monolithic ceramic cutting tools is increasing due to their great resistance to deformation at higher machining speeds and their good thermal stability. A major material is silicon nitride.^[5] The material is especially recommended for the high-speed machining of cast iron due to its excellent thermal stability, hardness, and wear resistance. When coated with TiN (by CVD), it is suitable for the machining of steel, since TiN provides further improvement in chemical resistance.^[6]

Other ceramic cutting-tool materials include alumina, Si-Al-O-N, alumina-carbide composites and, more recently, a composite of silicon nitride reinforced with silicon carbide whiskers. This last material can be produced by chemical-vapor infiltration (CVI) and has high strength and toughness as shown in Table 18.3.^[7]

Table 18.3

Selected Properties of Commercial Ceramic Cutting Tools

Material	Hardness GPa (KHN)	Fractur Toughness MPam	Rupture Modulus MPa	Thermal Conduct. W•m K	Coeff. of Thermal Expansion m/m.°Cx10 ⁻⁶
Al ₂ O ₃ *	15.6	2.9	280	32.3	8.22
Al ₂ O ₃ /TiC**	16.2	3.5	450		8.7
Al ₂ O ₃ /SiC***	17.0	6.0	675	35.2	7.35
Si ₃ N ₄ /20% SiC whiskers ****	13.0	6.0	1050	39.5	3.0

*	Kennmetal designation K060
**	NGK designation NTK-HC2
***	Greenleaf designation WG-300
****	GTE Valenite designation Quantum 6

These ceramics are usually coated by CVD with an appreciable increase in performance as shown in Fig. 18.1. A major use of these coated ceramics is in the machining of hard materials such as cast iron and superalloys.^[8]

4.4 Diamond Cutting Tools

Diamond, as single crystal or as a polycrystalline compact (PCD) is an excellent cutting material but is expensive and requires closely controlled speed and absence of chatter and vibration for optimum performance.^[9] It has limited oxidation resistance as it begins to oxidize in dry-grinding operations between 500 and 700°C, and the use of coolant is recommended to remain below these tem-

peratures. In addition, diamond reacts at approximately 1000°C with elements which are carbide formers such as iron, cobalt, nickel, aluminum, tantalum, and boron and is generally considered unsuitable to machine these materials. Diamond is normally used uncoated.

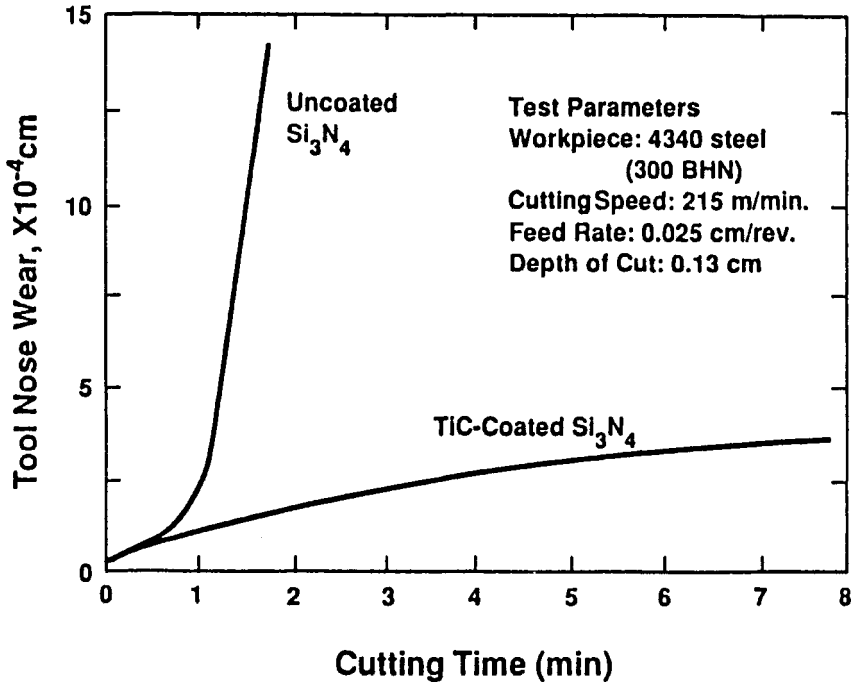


Figure 18.1. Wear of coated and uncoated ceramic tools.

4.5 Cubic Boron Nitride (c-BN) Cutting Tools

Cubic boron nitride is obtained from hexagonal boron nitride at high pressure and temperature in the presence of lithium nitride as a catalyst. It is almost as hard as diamond and has superior chemical resistance and a much higher oxidation threshold.^[10] Efforts to

produce c-BN in powder form or as a coating at low pressure by CVD have not been successful so far. Cubic boron nitride has remarkable properties: extreme hardness, toughness, chemical, and oxidation resistance and, rightly so, it is promoted as the cutting tool of the future.

5.0 CUTTING-TOOL MATERIALS (COATINGS)

5.1 Titanium Compounds

Most cutting-tool ceramic coating materials are titanium compounds, either binary or tertiary carbides and nitrides (see Ch. 9 and 10). These include TiN, TiC, TiCN, and TiAlN. Other ceramic coating materials are CrN for chemical resistance to copper and its alloys, molybdenum disulfide (MoS_2) for lubricity, and alumina (Al_2O_3) for corrosion and oxidation resistance. Many of these coatings are hybrid multilayer combinations in various sequences to meet specific cutting requirements. Selection of the optimum coating material (or combination of materials) depends on the type of machining operation, the material to be machined and other factors. The relative cutting performance of these coatings is given in Tables 18.4 and 18.5.^{[11]–[13]}

Table 18.4
Relative Cutting Performance of Coatings
for High-speed Steel Tools

Applications	Performance		
	Good	Better	Best
High and low alloy steels and stainless steel at medium and high cutting speed	TiN	TiCN	TiAlN
High and low alloy steels and stainless steel at low cutting speed and interrupted cuts	TiN	TiAlN	TiCN
Aluminum and Al/Si alloys, cast aluminum		TiAlN	Diamond DLC
Copper, brass, bronze			CrN
Titanium-based alloys			TiAlN
Nickel-based alloys			TiAlN

Table 18.5
Coating Materials for Cemented-Carbide Tools

Unalloyed steel	TiCN, TiAlN
Stainless steel	TiCN, TiAlN
Cast Iron	TiAlN
Al-wrought alloys	TiN
Al-cast alloys	TiCN
Copper	CrN
Brass	TiCN
Bronze	TiCN

The main applications of coated cemented carbides are tips and blanks, indexable inserts, milling tools, turning, and boring tools and circular saws.

5.2 Diamond and DLC Coatings

Coatings of polycrystalline CVD-diamond and diamond-like-carbon (DLC) are now entering the market of cutting and grinding applications (see Ch. 7). These materials have a great deal of potential but their applications are still mostly in the R&D stage. One such application is the coating of tungsten-carbide substrate. Adhesion may be a problem if cobalt (the binder material) is present on the surface since, in its presence, graphite will be formed instead of diamond. Reducing the amount of cobalt in the WC compact seems to eliminate the problem. These coatings have improved the flank wear of tools by a factor of 2–5. Initial use is for cutting aluminum and reinforced plastic. Diamond is also deposited on bulk silicon-nitride tools with much improved performance.

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19

CVD in Fiber, Powder, and Monolithic Applications

1.0 INTRODUCTION

The applications of CVD considered in the previous six chapters are related to coatings that are used to modify or enhance the surface properties of the substrate. In this chapter, the CVD applications which are not directly related to coatings are reviewed. They can be divided into the following categories: fibers, powders, monolithic shapes, and composites. Coatings form the great majority of CVD applications, the rest being shared more or less equally by each of these three categories. This amount, while small, is not negligible and may well increase as some of the present experimental applications become commercially viable.

2.0 CVD IN FIBER APPLICATIONS

CVD is used in the industrial production of inorganic structural fibers such as boron and silicon carbide. Boron fibers are, in

fact, one of the earlier commercial applications of CVD since the feasibility of the process and the superiority of the product were demonstrated as far back as 1959.^[1] CVD is also being considered for the production of several other types of metal and ceramic fibers.

2.1 Competing Processes

The process competes with the traditional method of fiber production in which the precursor material is melted, usually in an arc furnace, then drawn through spinnerets and spun or impinged by high pressure air. The melt-spin process is not well suited to materials with high melting points such as zirconia, silicon carbide, or pure alumina.

SolGel. A more recent competitor is the solgel process where the fibers are produced from a chemical solution, usually an alkoxide or mixed alkoxides, which is partially thickened by polymerization or by additives. The solution is spun directly into fibers or extruded through spinnerets and the resulting fibers are dried and sintered. Solgel does not require the high temperature of the direct-melt process and is being used successfully in the commercial production of several types of mixed-oxides fibers and in the production of silicon carbide fibers.^{[2][3]} Both CVD and sol-gel have their own advantages and drawbacks and, at this stage of development, it is not possible to forecast which one will prevail. It is likely that solgel will be the preferred process for oxide fibers and CVD for carbide, nitride, and boride fibers.

2.2 Materials and Applications of Inorganic Fibers

Table 19.1 summarizes the processes, characteristics and applications of commercial inorganic fibers.

This table (and Table 19.2 below) shows that the major competitor to CVD SiC is carbon as both fibers have similar properties and are in the same cost bracket. Another competitor is boron but it is expensive and may eventually be replaced by silicon carbide.

Table 19.1
Characteristics and Applications of Inorganic Fibers

Material	Processing	Main Characteristics	Typical Applications
Glass	Melt blowing and spinning	High strength Low modulus Low temperature Low cost	Insulation Reinforced plastics
Oxides	Melt spinning Sol-gel	Medium strength Good oxidation resistance High cost	Ceramic composites High-temp insulation Filtration
Boron	CVD	High strength High modulus High cost	Plastic and metal composites
Carbon	Pyrolysis	High strength High modulus Low density Low oxidation resistance Medium cost	Reinforced plastics Carbon-carbon High-temp insulation
Silicon carbide	CVD Sol-gel	High strength High modulus High cost	High-temp composites

2.3 The CVD Process for Fiber Production

Two fibers are presently produced by CVD on a commercial scale: boron and silicon carbide. The production of these two fibers requires a monofilament starter core capable of being heated resistively such as a tungsten or graphite fiber.^[4] The deposition apparatus is shown schematically in Fig. 19.1.

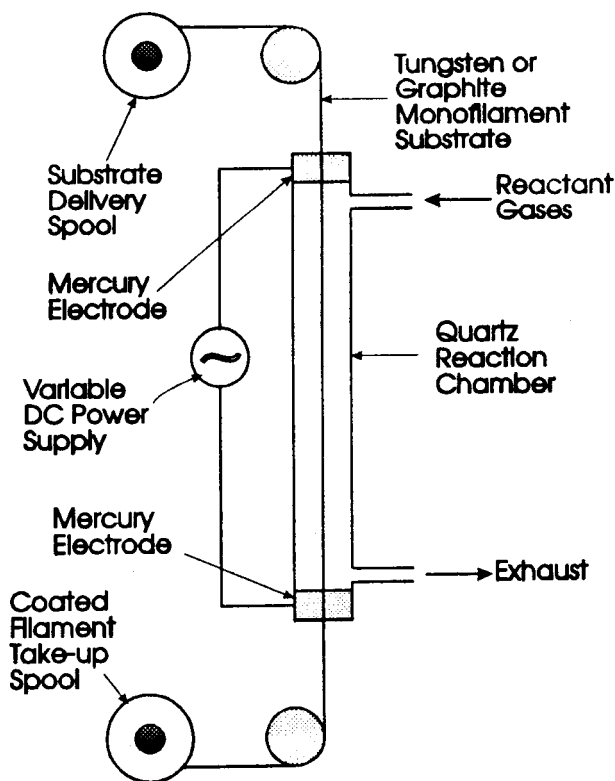


Figure 19.1. Apparatus for the deposition of silicon-carbide fibers.

Since a core is required, it is not possible to produce fibers with a small diameter and present production diameters are in the range of 100–150 μm , compared to an average of 10–20 μm for solgel derived fibers. Being very stiff with a high Young's modulus

and large diameter, they cannot be bent to a small radius or along compound shapes. They are difficult to weave into fabrics. Their use is limited to parts having a simple geometry such as plates, rods, or tubes.

A new process based on laser CVD does not require a core material and is able to produce fibers with a much smaller diameter. Deposition rate is up to 1 mm/sec. The process is still experimental and is presently being developed for the production of boron, SiC, and Si₃N₄.^[5] The core-less deposition may be accomplished by impinging the laser beam on the growing end of a retreating fiber in a CVD atmosphere.

2.4 The CVD of Boron Fibers

Processing. The CVD reaction used to produce boron fibers is the hydrogen reduction of boron chloride (see Ch. 8).^{[4][6]} At the deposition temperature of 1300°C, the tungsten core reacts rapidly with the deposited boron to form the brittle tungsten borides W₂B₅ and WB₄. No metallic tungsten remains. The “boron” fiber actually consists of a boron envelope surrounding a tungsten boride core which typically occupies 5% of the fiber cross section.

Properties. CVD boron fibers have high strength, high modulus, and low density. Their properties are summarized and compared with SiC fibers and other inorganic fibers in Table 19.2 (data supplied by the manufacturers).

The drawbacks of boron fibers are:

- A tendency to further grain growth at high temperature.
- The high reactivity of boron with many metals and the formation of brittle intermetallic phases.
- High cost.

The reactivity problem can be partially remedied with the use of intermediate coatings (see Sec. 2.5 below).

Table 19.2
Tensile Strength, Modulus, and Density
of Selected Inorganic Fibers

Major Constituent	Tensile Strength (MPa)	Tensile Modulus (GPa)	Density (g/cm ³)	Fiber diam. (μ m)
Glass (a)	4580	86	2.5	10
Alumina (b)	1750	154	2.7	10–20
Alumina (c)	2275	224	3.0	10–20
Boron (d)	3600	400	2.5	100
Carbon (e)	5500	330	1.8	6–10
Sol-gel SiC (f)	3400	165–200	2.57	10–20
CVD SiC (g)	3920	406	3.0	140

(a) S-Glass, Corning Glass, Corning, NY

(b) Nextel 312, 3M, Minneapolis, MN

(c) Nextel 400

(d) Avco Boron

(e) MS-40, Grafil, Sacramento, CA

(f) Nippon Carbon, Tokyo, Japan

(g) Avco SCS 6, Textron Inc., Lowell, MA
(carbon-fiber substrate)

Applications. Boron fibers are used as unidirectional reinforcement for epoxy composites in the form of preimpregnated tape. The material is used extensively, mostly in fixed and rotary wing military aircrafts for horizontal and vertical stabilizers, rudders, longerons, wing doublers, and rotors. They are also used in sporting goods. Another application is as reinforcement for metal matrix composites, in the form of an array of fibers pressed between metal foils, the metal being aluminum in most applications.

Boron has high neutron absorption and the boron-aluminum composites are being investigated for nuclear applications. Single-ply boron-epoxy composites have microwave polarization properties with potential applications in antenna and radome designs.^[1]

2.5 The CVD of Silicon-Carbide Fibers

CVD silicon carbide fibers are a recent development with promising potential which may take over some of the applications of CVD boron fibers or other refractory fibers, providing that the production cost can be reduced.

Processing. The process requires a monofilament carbon-fiber core which is heated resistively in a tubular glass reactor shown schematically in Fig. 19.1.^[2] A carbon monofilament is pre-coated with a 1 μm layer of pyrolytic graphite to insure a smooth deposition surface and a constant resistivity.^[7] SiC is then deposited by the reaction of silane and a hydrocarbon. Other precursors such as SiCl_4 , and CH_3SiCl_3 are also being investigated.^[8] A fiber cross-section is shown in Fig. 19.2.^[9]

Properties. Properties of SiC fibers are shown in Table 19.2. They are similar to those of CVD boron fibers except that SiC is more refractory and less reactive than boron. CVD-SiC fibers retain much of their mechanical properties when exposed to high temperature in air up to 800°C for as long as one hour as shown in Fig. 19.3.^[8] SiC reacts with some metals such as titanium in which case a diffusion barrier is applied to the fiber (see Sec. 2.5 below).

Applications. Most applications of CVD SiC fibers are still in the development stage. They include the following:^{[10][11]}

- Reinforcement for metal-matrix composites with such metals as titanium, titanium aluminide, aluminum, magnesium, and copper. Applications are found mostly in advanced aerospace programs and include fan blades, drive shafts, and other components.
- Reinforcement for ceramic and polymer composites.

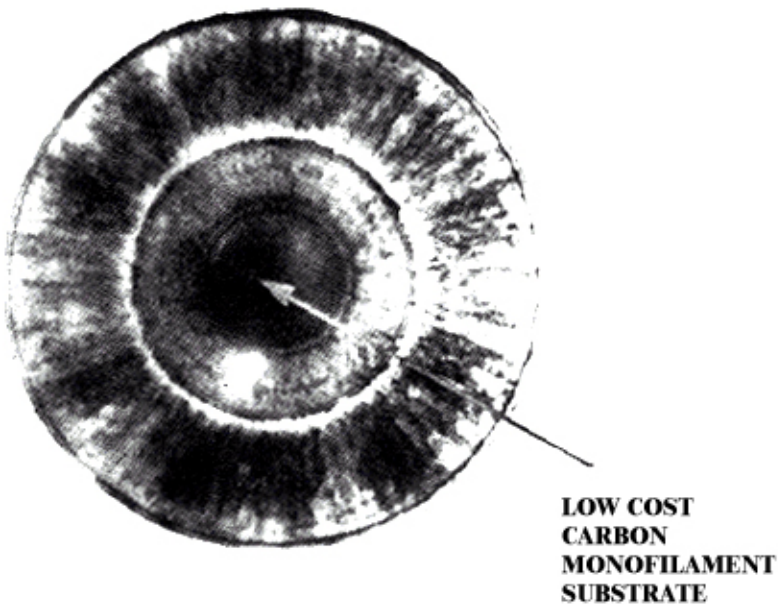


Figure 19.2. Cross section of a CVD silicon-carbide fiber, courtesy of Textron Specialty Materials.

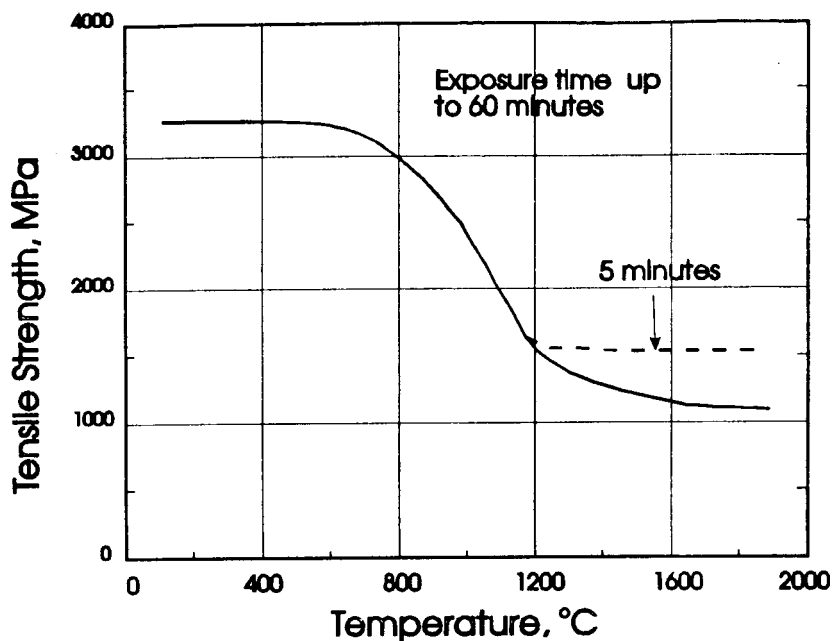


Figure 19.3. Tensile strength of CVD silicon-carbide fiber as a function of temperature.

2.6 Other Refractory-Fiber Materials

Other materials besides boron and SiC with potential for CVD fiber production are being investigated. They include B_4C , TiC, and TiB_2 deposited on a heated core filament, generally by the hydrogen reduction of the chlorides.^{[4][8][12]} Typical properties of the resulting experimental fibers are shown in Table 19.3. Fiber diameter varies from 20 to 200 μm .

Table 19.3
Selected Properties of CVD Fibers^[7]

	B ₄ C	TiC	TiB ₂
Melting Point, °C	2450	3180	2980
Deposition Temperature, °C	1300	1400	1250
Thermal Expansion, ppm/°C	5.0	7.6	7.9
Tensile Strength, GPa	2.07–2.76	1.38–2.07	1.38–2.07
Modulus, GPa	172–241	172–241	138–207

2.7 CVD Coatings for Fibers

Inorganic fibers, whether made by CVD, solgel, or other processes, may react with the metal or ceramic matrices during the processing of composites or during operations at high temperatures. Such reactions produce intermetallics or other compounds which may considerably degrade the properties of the fiber. In such cases, it is necessary to apply a coating on the fiber that acts as a diffusion barrier and prevents this diffusion reaction. The most common technique for applying such coatings is CVD.^[14] A typical fiber coating apparatus is shown schematically in Fig. 19.4. Common diffusion barrier materials are pyrolytic carbons, BN, TiN, TiB₂, SiC, and rare earth sulfides.^{[14]–[16]}

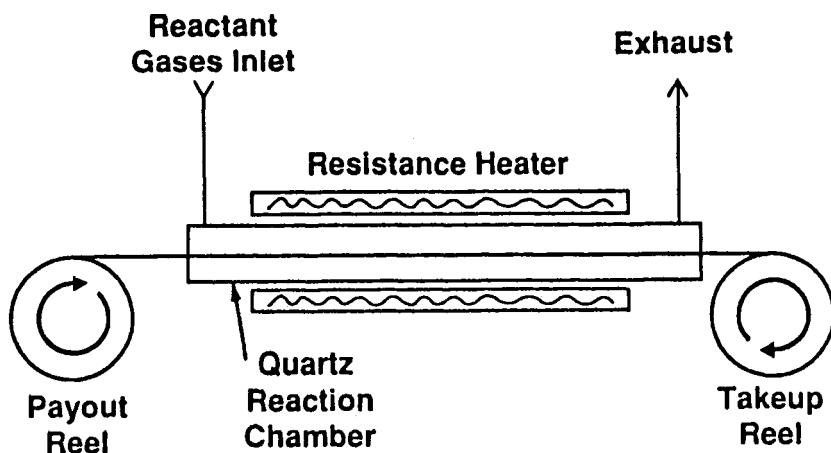


Figure 19.4. Schematic of CVD fiber coating apparatus.

2.8 Whiskers

Whiskers are short fibers, usually a single crystal with an aspect ratio of 10/1 or greater. They have high strength but are difficult to process. Their applications so far has been limited; SiC whiskers are reported as random reinforcement for ceramics and in alumina cutting tools. CVD is a common production method.^[17] Beside SiC, the following whiskers have recently been produced by CVD:

- Titanium diboride whiskers by the hydrogen co-reduction of TiCl_4 and BBr_3 in the presence of a platinum catalyst. These whiskers are 20–30 nm thick and 12–13 μm in length.^[18]
- Titanium carbide whiskers from TiCl_4 , CH_4 , and H_2 in the presence of a nickel catalyst at 1220–1450°C.^[19]

- Hafnium carbide and hafnium nitride whiskers from HfCl_4 , CH_4 or N_2 , and H_2 in the presence of a nickel catalyst at 1000–1450°C.^[20]

3.0 CVD IN POWDER APPLICATIONS

3.1 Ceramic-Powder Production

The general trend in ceramic powder technology is toward better batch-to-batch reproducibility of properties, improved physical or chemical properties and lower processing temperature. New materials such as silicon nitride, silicon carbide, and partially stabilized zirconia have strength which is achieved by using precursor powders with great purity, small particle size, uniformity, and freedom from aggregation. These powders are now used to produce a wide variety of ceramics such as structural components, catalyst supports, pigments, electro-optical and magnetic devices, drug-delivery carriers, and many others.

The traditional ceramic-powder preparation includes heating or calcination of the raw material, grinding and milling and dispersion. Although satisfactory for most purposes, these powders do not generally meet the exacting requirements of advanced ceramic applications. High-quality powders of refractory materials can be obtained by several processing techniques, RF-plasma torch, combustion synthesis, solgel, and especially CVD.^{[21][22]}

3.2 CVD Process for Ceramic-Powder Production

The preparation of ceramic powders by CVD is a promising and growing field. These powders are used as precursors for the processing of advanced ceramics, or directly as powder for such applications as abrasives.

If the temperature and supersaturation are sufficiently high in a CVD reaction, the product is primarily powder precipitated from the gas phase (see Ch. 2). Such powders have few impurities provided that the CVD precursors are carefully purified. Their small diameter and great uniformity are important factors in the production of high quality hot-pressed or sintered ceramic bodies with good mechanical and electrical properties. In addition, the sintering temperatures required for CVD powders are lower than those for conventional powders.

The following powders are made experimentally or on a production basis.

- Beta SiC powder from the decomposition of methyltrichlorosilane (MTS) in the presence of hydrogen in an argon plasma. Also from the gaseous thermal decomposition of tetramethylsilane, $\text{Si}(\text{CH}_3)_4$, in a flow-through reactor between 850 and 1500°C^[23] and by the reaction of acetylene and silane.
- Submicron β -SiC powder by reacting silane and acetylene in a 10–50 W continuous-wave CO_2 laser beam.^[24]
- Amorphous Si_3N_4 powder from silicon halides and ammonia at high temperature.^{[25][26]} The powder can also be produced by using the same reaction at 1000°C in an RF plasma with a mean particle size of 0.05–0.1 μm .^[27]
- Si_3N_4 powder by laser CVD from halogenated silane and ammonia with an inert sensitizer such as SF_6 .^[28]
- Aluminum nitride submicron powder from aluminum alkyl^[25] and from the reaction of aluminum powder, lithium salt, and nitrogen at 1000°C.^[29]
- Magnesium oxide powder from magnesium vapor and oxygen,^[30] and tungsten carbide.^[30]

Applications. CVD ceramic powders such as SiC and Si₃N₄ are used to produce ceramic bodies for a wide variety of applications, either experimentally or in production. These include structural applications in high temperature or corrosive environments where metals are not suitable, in such areas as reciprocating engines, gas turbines, turbochargers, bearings, machinery, and process equipment.

Another area is superconductivity where powders of YBa₂Cu₃O₇ produced by CVD are used in the fabrication of sputtering targets and may also be used in plasma spraying for the fabrication of superconductor wires and coatings (see Ch. 11). Rapidly growing in importance is the production of high thermal conductivity heat-sink material for integrated circuits from CVD AlN powders (see Ch. 10).

How much of an impact CVD ceramic powders will have on ceramic technology is not clear at this time since applications have yet to reach the commercial stage in any significant manner. Yet the success of a number of development programs suggests that CVD should become a major technology in this field. This is already evident in Japan which is the recognized leader in advanced ceramics.

3.3 CVD Metal Powders

The processing of metals by powder metallurgy has unique advantages and the resulting products have excellent properties.^[32] Several metal powders for powder metallurgy are now produced by CVD, mostly on an experimental basis. These include:

- Iron, nickel, cobalt, molybdenum, and tungsten powders produced by the pyrolysis of the respective metal carbonyl (see Ch. 3).^[33]
- Tungsten, produced from WF₆ to a purity in excess of 99.9995%.^[34]

3.4 Coated Powders by CVD

Both metallic and ceramic powders as small as 5 μm in diameter can be coated by CVD by the fluidized-bed technique with good uniformity (see Ch. 4). The most common coating materials are nickel and iron which are obtained by the decomposition of the respective carbonyl (see Ch. 3). These metals are used to coat tungsten particles to promote sintering in powder metallurgy applications.^{[35][36]} Sintering time, sintering temperature, and grain growth are reduced, contamination is lessened and properties are improved.

A major problem in fluidized-bed coating is particle agglomeration. As the particle size is decreased, it becomes more difficult to avoid agglomeration and to coat the particles individually. The tendency to agglomerate increases with decreasing density and with increasing temperature. It is also a function of the materials (substrate and coating), the particle shape (acicular vs. equiaxed), and the coating atmosphere (presence or absence of molecular species). The composition, configuration, and flow dynamics of the fluidizing atmosphere can be adjusted within limits to promote unagglomerated fluidization.

Other potential applications are ceramic powders coated with their sintering aids, zirconia coated with yttria stabilizer, tungsten carbide coated with cobalt, or nickel, alumina abrasive powders coated with a relatively brittle second phase such as MgAl_2O_4 and plasma spray powders without the segregation of alloying elements.

4.0 CVD IN MONOLITHIC AND COMPOSITE APPLICATIONS

Some of the earliest applications of CVD were monolithic (or free-standing) structures. A tungsten tube made by CVD was reported as early as 1932.^[17] The applications of CVD in this area are now well established and many are in substantial commercial production.

4.1 Graphite, Carbon-Carbon, and Boron Nitride CVD Structures

Pyrolytic Graphite. CVD graphite (also known as pyrolytic graphite) has a strong structural anisotropy and a corresponding anisotropy in its properties (see Ch. 7). It is used in applications which require high strength and corrosion resistance at high temperature in non-oxidizing environments. Such applications include crucibles, semiconductor wafer handling equipment, electrodes, reaction vessels for gas-phase epitaxy, and rocket nozzles.^[37]

Carbon-Carbon. Carbon-carbon composites consist of a carbon fiber substrate, either in the form of woven fabric or random felt, and a carbon matrix.^[37] The matrix is produced by the pyrolysis of a polymer, usually phenolic, reinfiltated by CVD or by chemical vapor infiltration (CVI) alone (see Ch. 7). The material has outstanding high temperature mechanical properties and excellent chemical resistance except to oxidation. It is a high cost material and its uses are mostly limited to aerospace at the present time. Some applications are as follows.

- Carbon-carbon has antigalling characteristic with the ability to slide against itself with very little wear, making it ideal for high-performance brakes. Such brakes are probably the major application of carbon-carbon and are found on most military aircraft, on the space shuttle. They are being introduced on civilian aircraft and racing cars.^[38]
- The space shuttle and other aerospace vehicles use carbon-carbon extensively in nose cap, leading edges, structural panels, and other components.
- Experimental gas turbine rotors have demonstrated the potential of carbon-carbon provided that the oxidation problem can be solved.
- Other applications include missile nozzles and nose cones, aerospace fasteners, heating elements, and glass bottle machinery components.

Boron Nitride. Pyrolytic boron nitride (PBN) produced by CVD is inert chemically and, like pyrolytic graphite, has highly anisotropic properties (see Ch. 10). For instance, its thermal conductivity in the a-b direction is 40 times that of the c direction. It is much more oxidation resistant than graphite. As such, it is an ideal material for high temperature containers and is manufactured commercially in the form of crucibles for aluminum evaporation and molecular-beam epitaxy, Czochralski crystal-growth vessels of III–V and II–VI compounds and general furnace hardware. It is also produced as an insulating substrate in ribbon heaters in combination with a pyrolytic graphite resistance heating element.^{[39][40]}

4.2 Monolithic Metallic Structures

Many refractory metals are difficult to fabricate by conventional metallurgical processes because of their high melting point. They are usually hard and brittle due to the presence of impurities which makes them difficult to machine. It is possible to produce these metals by CVD to near net shape and minimize the need to machine them. In addition, CVD produces metals which can be made to a high degree of purity (greater than 99.9%) and minimize the inclusion of carbon, oxygen, or other contaminants that are the major cause of embrittlement in powder metallurgy processing of refractory metals.

The refractory metals for which CVD is commonly used to produce free-standing shapes are tungsten, niobium, rhenium, tantalum, molybdenum, and nickel^{[17][41][42]} (see Ch. 6). Shapes presently produced include rods, tubes, crucibles, manifolds, ordnance items, nozzles, and thrust chambers. They are usually deposited on a disposable mandrel of copper, molybdenum, or graphite which is subsequently machined off or removed chemically by etching.

4.3 CVD Ceramic Composites

The major drawback of ceramics is their intrinsic brittleness. For example, most metals have a fracture toughness forty times greater than

conventional ceramics and glasses. This brittle characteristic is related to the strong hybrid ionic-covalent bonds of ceramics. These high-strength bonds prevent energy-absorbing deformation which occurs in ductile metals. Since ceramics cannot deform, they fail catastrophically. Applied stresses tend to concentrate at the sites of flaws such as voids, notches, scratches, or chemical impurities at grain interfaces.

Ceramic composites, which use ceramic fiber or whisker reinforcement in a ceramic matrix, are less susceptible to brittle failure since the reinforcement intercepts, deflects and slows crack propagation. At the same time, the load is transferred from the matrix to the fibers to be distributed more uniformly. These ceramic composites are characterized by low density, generally good thermal stability, and corrosion resistance.

Actual strength measurements are still a long way from their theoretical strength because of the non-ductile behavior of the matrix which results in pronounced notch sensitivity and leads to catastrophic failure. The development of suitable CVD intermediate coatings between fiber and matrix allows a certain degree of load transfer to the fiber, and has improved mechanical properties to some extent. However, exposure to high temperature (i.e., $>1000^{\circ}\text{C}$) causes diffusion and chemical bonding across the interface and brittle failure is still dominant. A great deal of experimental work is under way to remedy these conditions.

The reinforcing fibers are usually CVD SiC or modified aluminum oxide. A common matrix material is SiC deposited by chemical-vapor infiltration (CVI) (see Ch. 5). The CVD reaction is based on the decomposition of methyl-trichlorosilane at 1200°C . Densities approaching 90% are reported.^[43] Another common matrix material is Si_3N_4 which is deposited by isothermal CVI using the reaction of ammonia and silicon tetrachloride in hydrogen at $1100\text{--}1300^{\circ}\text{C}$ and a total pressure of 5 torr.^[44] The energy of fracture of such a composite is considerably higher than that of unreinforced hot-pressed silicon nitride.

To this date, the fabrication of structural ceramic composites has been limited to prototypes mostly in high-cost, high-performance aerospace applications such as missile guidance fins, hypersonic fuselage skins, inner flaps, and rocket nozzles.

If the composite is left only partially densified, it can be used as a filter for high temperature filtering systems with high collection efficiency as required in direct coal-fired gas and steam turbines.^[38] Similar systems are considered for particulate filtering in diesel engines by a carbon foam or felt coated with silicon carbide by CVI.

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Appendix: Alternative Processes for Thin-Film Deposition and Surface Modification

Chemical vapor deposition competes directly with other coating processes which, in many cases, are more suitable for the application under consideration. These competing processes comprise the physical vapor deposition (PVD) processes of evaporation, sputtering, and ion plating, as well as the molten-material process of thermal spray and the liquid-phase process of solgel. A short description of each process follows. For greater detail, the listed references should be consulted.

1.0 PHYSICAL VAPOR DEPOSITION (PVD)

Like CVD, PVD is a vapor deposition process where the deposition species are atoms, molecules, or a combination of the two. The distinction between these two processes is that, in CVD, deposition occurs by chemical reaction, whereas in PVD, deposition is by condensation. CVD is usually endothermic and PVD is exothermic.

An important recent trend is the tendency for the two processes, CVD and PVD, to merge. CVD for instance, now makes extensive use of plasma (a physical phenomenon) and conversely,

reactive evaporation and reactive sputtering occur in a chemical environment. CVD and PVD reactors are now combined in one single piece of equipment in new semiconductor processing operations and the difference between the two processes becomes blurred.

The three principal PVD subprocesses, evaporation, sputtering, and ion plating, are described below^{[1][2]}

2.0 EVAPORATION

2.1 Principle of Evaporation

The principle of evaporation is relatively simple. The coating material (known as the source) is heated at low pressure ($<10^{-3}$ Pa) above its boiling point, sending atoms or molecules through a cosine distribution of trajectories in a straight line to the substrate, where these condense to form a thin film. At such low pressure, the mean-free path is large compared to the distance between the source and substrate and few collisions occur before the species condense on the substrate. This leads to uneven thickness buildup since the thickest part of the coating will be that which is closest to the source. To compensate for that, planetary substrate holders and multiple sources may be used. High deposition rates are now possible and may reach 75 $\mu\text{m}/\text{min}$. The drawbacks of evaporation are generally poor adhesion of the coating and difficulty in coating complex shapes.

To evaporate the source material, various heating methods are used such as resistance heating, electron beam, pulsed excimer laser, or cathodic arc (where the source is the cathode).

2.2 Reactive Evaporation

Compounds such as the refractory carbides, nitrides, and oxides have extremely high boiling points and generally dissoci-

ate during evaporation. The condensation of the molecular fragments on the substrate depends on many factors and the stoichiometry of the deposit may be different from that of the source. To minimize this problem, the process known as *reactive evaporation* is used where the nonmetallic element of the coating (carbon, nitrogen, or oxygen) is introduced into the gas phase and a pure metal source is used. For instance, TiN is deposited when a titanium target is evaporated in an atmosphere of nitrogen or ammonia. Likewise, to produce a carbide, evaporation occurs in a hydrocarbon atmosphere. As with CVD, the reaction must have a negative free energy of formation ($-\Delta G^\circ$) in order to proceed. Fortunately, this is usually the case.^[3]

2.3 Plasma Evaporation

In some cases, the deposition rate can be increased by the action of a plasma in a process known as *activated reactive evaporation* (ARE).^[3] The plasma enhances the reactions and modifies the growth kinetics of the deposit.

2.4 Molecular Beam Epitaxy

Another evaporation technique is molecular beam epitaxy (MBE). MBE produces extremely pure and very thin films with abrupt composition changes and is being considered for extremely exacting electronic and optoelectronic applications.^[4] However, the deposition rate is very slow and the process is still considered experimental.

2.5 Typical Applications of Evaporation

Evaporation is used extensively for the deposition of aluminum and other low melting-point metals as well as hard coatings such as TiN for cutting tools, decorative coatings (jewelry), and for the metallization of paper and fibers. It is also a major coating

process for optical applications. Large, continuous coating equipment is now available.^[3] Evaporation is facing strong competition from CVD and particularly sputtering.

3.0 SPUTTERING

Sputtering is an important thin-film process used extensively in the semiconductor and hard-coating industries and for decorative and jewelry coatings.^{[5][6]} Excellent coatings of refractory compounds and metals can be readily produced with good adhesion and composition control without the high temperature requirements of CVD.

3.1 Principle of Sputtering

A source (or target) is placed in a high vacuum and bombarded with gas ions (usually argon) which have been accelerated by a high voltage, producing a glow discharge or plasma. Atoms from the target are physically ejected by momentum transfer and move across the vacuum chamber to be deposited on the substrate. Unlike CVD or evaporation, the process is not thermally activated.

The disadvantages of sputtering are a relatively low deposition rate and a line-of-sight deposition characteristic which makes the coating of deep holes and trenches difficult. This can be overcome to some extent by operating at higher pressure (but at some sacrifice in deposition rate) or by the use of three-dimensional grids. On the other hand, the high energy of sputtered particles improves adhesion and produces a denser and more homogenous coating than evaporation.

Low-Pressure Requirements. Sputtering requires low pressure to remove all traces of background and contaminant gases which could degrade the coating. This is achieved by cryogenic pumps capable of producing a vacuum of 10^{-5} Pa with good pumping speed. After evacuation, the system is refilled with argon to a partial pressure of 0.1 to

10 Pa. Higher pressure, by placing too many argon atoms in the path of the ions and ejected atoms, would not allow these to travel relatively unimpeded by collision. In other words the mean-free path would be too short.

3.2 Reactive Sputtering

Like reactive evaporation, reactive sputtering is used in the deposition of refractory compounds by providing a small partial pressure of hydrocarbons, nitrogen, or oxygen. A problem is target poisoning caused by the reaction of the target with the reactive gas.

3.3 Sputtering Techniques

Several techniques are used in sputtering:

- *Diode sputtering* is the simplest but requires an electrically conductive target; it has low energy efficiency and electron bombardment may cause significant damage of the substrate.
- *Radio-Frequency (RF)* sputtering, using frequencies above 50 kHz, can sputter insulators but the process has low deposition rates.
- *Triode sputtering* uses an additional cathode to sustain the plasma but is more complicated and may cause contamination of the deposit.
- *Magnetron sputtering* uses a magnetically enhanced cathode (magnetron). This process has considerably expanded the potential of sputtering. The magnetron sends the electrons into spiral paths to increase collision frequency and ionization. Deposition rates are high and the process does not cause radiation damage.

3.4 Examples of Sputtered Films

- Insulators and diffusion barriers for semiconductor devices.
- Hard coatings for cutting tools and erosion applications.
- TaN resistive films for hybrid circuits deposited by planar magnetron sputtering.
- Metallization of semiconductor devices (W, Cu, Al).

4.0 ION PLATING

In ion-plating deposition, the substrate and the deposited film (as it forms) are subjected to bombardment by particles (ions, atoms, molecules) which alter the formation process and the properties of the coating.^{[7][8]} The process is also called *ion-beam assisted deposition* (IBAD).

Two basic versions of the process: plasma-based ion plating and vacuum-based ion plating. The coating material is vaporized in a manner similar to evaporation. Typically, the plasma is obtained by biasing the substrate to a high negative potential (5 kV) at low pressure. The constant ion bombardment of the substrate sputters off some of the surface atoms which results in improved adhesion and reduced impurities. Surface coverage of discontinuities is also improved.

Reactive ion plating is similar to reactive sputtering and evaporation with applications in optical, wear, abrasion, lubrication, and decorative coatings.

5.0 THERMAL SPRAY

5.1 Principle of Thermal Spray

Thermal spray is a well-established, relatively low-cost, industrial processes which is used widely for the deposition of metals and compounds, including the refractory carbides and nitrides. Examples are coatings of tungsten carbide with a cobalt binder which are of major industrial importance.^[9]

The coating material, usually in the form of powder, is metered into a compressed-gas stream and fed into the heat source where it is heated to its melting point and projected onto the substrate. In the case of refractory metals and compounds which have high melting points, spraying is carried out in an inert atmosphere to avoid detrimental chemical reactions such as oxidation.

The properties of thermal-sprayed coatings vary as a function of processing parameters such as temperature and particle velocity. Generally, such coatings have greater porosity than CVD or PVD coatings and thickness control is more difficult to achieve. Yet the process is economical and undemanding. It can be applied in any location.

5.2 Heat Sources

Various heat sources are available including:

- Detonation gun (D-gun) which uses the energy of continuous, controlled explosions of oxyacetylene mixtures to obtain the necessary kinetic energy.
- High-velocity oxy-fuel (HVOF) which operates at high pressure (10 MPa) and high particle velocity (ca. 315 m/s).
- Plasma spray using a dc-plasma torch or a RF inductively coupled torch.

5.3 Reactive Thermal Spray

Coatings of refractory compounds can be deposited reactively in a manner similar to reactive evaporation and sputtering by spraying the pure metal in an atmosphere of either a hydrocarbon or nitrogen.

5.4 Typical Applications

Most metals and many refractory compounds can be thermal-sprayed. Applications include coating of gas-turbine components for aircraft and industrial use, components of steam turbines and diesel engines, components for the oil and gas industry, paper and pulp industry, and chemical processing industry.

6.0 SOLGEL

Solgel processing or, more broadly speaking, the processing of ceramics and glasses from chemical precursors, is an emerging technology with a great potential especially in coatings and fiber production. At present, the development of solgel is still predominantly in the laboratory, yet it has spurred a great deal of interest in high-technology industries such as semiconductors, optoelectronics, optics, and structural ceramics. Solgel is already used in a sizable range of applications particularly in thin films. These applications include the spin-on-glass (SOG) process which is used in semiconductor fabrication and the coating of architectural glass to control optical properties.^[10]

The solgel process uses a liquid reactive precursor material that is converted to the final product by chemical and thermal means. This precursor is prepared to form a colloidal suspension or solution (sol) which goes through a gelling stage (gel) followed by drying and consolidation. The process requires only moderate temperatures, in many cases less than half the conventional glass or ceramics

processing temperatures. It also permits very close control of the composition and structure of the deposit on the molecular level and makes possible the production of near-net shapes. These are very important advantages.

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